ORGANOALUMINUM INTERMEDIATES IN THE SYNTHESIS OF ALLYL- AND VINYL-SILANES

By

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To the mighty God of this universe,
my parents, my sister and my friends, who
support and encourage me

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"Dear friends, let us love one another, because love comes from God. Whoever loves is a child of God and knows God. Whoever does not love does not know God, for God is love. And God showed his love for us by sending his only Son into the world, so that we might have life through him. This is what love is: it is not that we have loved God, but that he loved us and sent his Son to be the means by which our sins are forgiven." 1 John 4: 7-10.

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Abstract of Dissertation Presented to the Graduate School
of the University of Florida in Partial Fulfillment of the
Requirements for the Degree of Doctor of Philosophy

ORGANOALUMINUM INTERMEDIATES IN
ALLY- AND VINYL- SILANES SYNTHESIS

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Major Department: Chemistry

Many methodologies have been developed for the preparation of allyl- and vinyl-silanes, but most of the existing methods involved at least two or more synthetic steps. We have developed a convenient one-pot reaction to produce either allyl- or vinyl- silane.

Tris(trimethylsilylmethyl)aluminum lithium bromide complex ***2-1***, a selective Peterson olefination reagent, reacted with benzophenone at elevated temperatures to afford (2,2-diphenylvinyl)trimethylsilane, ***2-4***, reactions of ***2-1*** with other ketones afforded unsatisfactory results. Therefore, the methodology was extended to employ 1.2 eq. of $LiCH_2TMS$ (for non-enolizable ketones) or 1.5 eq. of $LiCH_2TMS/CeCl_3$ (for enolizable ketone) to fulfill the initial alkylation step to the carbonyl group with xylene as solvent. Reaction mixtures were allowed to reflux (24 to 96 hours) after

subsequent addition of 1.4 eq. of diethylchloroalane followed by introduction of 0.1 eq. of 1 M H_2O in THF (to generate a catalytic amount of alumoxanes) to produce either vinylsilanes or allylsilanes. In general, reactions of non-enoliazable aromatic ketones afforded the corresponding vinylsilanes as major products in fair to good yields with high chemo- and stereoselectivity, while, reactions of enolizable ketones afforded the corresponding allylsilanes as major products in respectable yields with high regioselectivity.

The reaction mechanism is believed to proceed through an intramolecular E1-like pathway producing carbocations as the reactive intermediate. This conclusion is supported by the formation of an addition (ethylation) product in the reaction of xanthone and formation of 5-phenyl-10,11-dihydro-5*H*-dibenzo[*a,d*]cycloheptene. In both cases, the carbons containing hydroxy group are tertiary centers. In order to substitute the oxygen, cations must have formed prior to the ethylation or reduction. The formation of the ethylation and the reduction product strongly suggested that these elimination reactions producing vinylsilanes or allylsilanes proceed through a E-1 like pathway rather than E2-like or syn-cyclic mechanisms. In summary, a useful one-pot procedure for the formation of allyl- vinyl-silanes from ketones has been developed.

CHAPTER 1
INTRODUCTION

Allyl- and vinylsilanes are silicon-containing olefins. Silicon alters the reactivity of the double bond of allyl- and vinylsilanes; therefore, they are valuable synthetic intermediates. There is a great deal of methodology for the preparation of these types of compounds, but very few of the available methods involve one-pot synthesis and are mediated by organoaluminums. The goal of this dissertation is to report a new convenient, one-pot synthesis involving organoaluminum promoted E1-like elimination to produce allyl- and vinylsilanes.

Historical Background and Properties of Aluminum

In the earth's crust, the third most abundant element is aluminum. It is a ductile, malleable and bluish-white metal, which was first discovered by Antoine Lavoisier in 1787, named by Sir Humphry Davy in 1807, and isolated in pure form by Hans Christian Orsted in 1825. Aluminum belongs to Group IIIA on the periodic table; therefore, the principal oxidation state of aluminum is + 3 (Table 1-1). Among its eleven isotopes with atomic weights between 22 and 31, aluminum-27 is 100 % naturally abundant.[1] The remaining isotopes are artificial and radioactive.

Table 1-1. Properties of aluminum.

Element	Aluminum
Electron Configuration	Ne $3s^2 3p^1$
Atomic number	13
Atomic weight	26.9815
Melting point	660.37 °C
Boiling point	2467 °C
Oxidation state	+ 3
Specific Gravity	2.699 @ 20 °C
Ionization Energies[2]	5.98, 18.82, 28.44, 153.77 eV

Production of aluminum and its derivatives

Pure aluminum can be obtained via the Hall Process which involves electrolysis of aluminum oxide, Al_2O_3, from natural bauxite. In the Hall process, a liquid mixture of aluminum oxide, cryolyte, and fluorite (cryolyte and fluorite are used to lower the melting point of aluminum oxide) is electrolyzed to afford aluminum metal and oxygen gas (equation 1-1).

$$2Al_2O_3 \rightarrow 4Al + 3O_2 \qquad \textbf{equation 1-1}$$

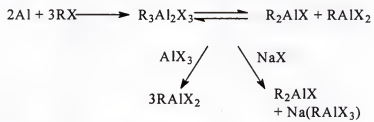
Pure aluminum is a bluish-white, highly malleable, and ductile metal. Aluminum metal is protected by its outside oxide coating and, therefore, resists oxidation. However, without its protective oxide layer, the low ionization energy of aluminum makes it readily

oxidized by various of chemicals to a +3 oxidation state. Thus, organoaluminums can be made by reactions of pure aluminum with alkylhalides through redox reactions.

Organoaluminum compounds are pyrophoric. Standard techniques for handling air-sensitive materials are necessary when one prepares or handles organoaluminum substances. Organoaluminum compounds are usually of the following types: triakylaluminum (R_3Al), dialkylaluminum halides (R_2AlX), and alkylaluminum dihalides ($RAlX_2$), where R can be an alkyl, alkenyl, aryl, or alkynyl groups.

Alkylaluminum halides

Alkylaluminum halides can be prepared from the reactions of sesquihalide ($R_3Al_2X_3$) with sodium halides (NaX) to afford the corresponding R_2AlX species or with stoichiometric amounts of aluminum halides (AlX_3) to produce the corresponding $RAlX_2$ derviatives (Scheme 1-1).[3]



Scheme 1-1

Dialkylaluminum hydrides

Ziegler and co-workers developed a direct synthesis of dialkylaluminum hydrides (R_2AlH) involving the reaction of a trialkylalane, activated aluminum, and hydrogen under pressure at elevated temperature (equation 1-2). An alternative method is to extrude an olefin by β-hydride transfer from trialkylalane at elevated temperatures, as shown in equation 1-3.

$$2R_3Al + 1.5\ H_2 + Al \rightarrow 3R_2AlH \qquad \textbf{equation 1-2}$$

$$i\text{-}Bu_3Al \rightarrow i\text{-}Bu_2AlH + CH_2{=}C(CH_3)_2 \qquad \textbf{equation 1-3}$$

Trialkylalanes

Industrial preparation. In addition to the method involving a reaction of aluminum with excess of alkylhalide to produce trialkylaluminums. Reactions of aluminum metal and hydrogen with olefins under special conditions provides an industrial synthesis of trialkylalanes.[4]

Reaction of dialkyl mercury with aluminum metal. For small-scale preparations, trialkylalanes can be obtained from the reaction of mercury dialkyls with aluminum metal at elevated temperature (equation 1-4). Unfortunately, secondary and tertiary trialkylaluminums tend to isomerize to primary derivatives at elevated temperatures, thus imposing some limitations on this method. [3,5]

$$2Al + 3HgR_2 \rightarrow 2AlR_3 + 3Hg \qquad \textbf{equation 1-4}$$

Ligand exchange reaction between trialkylalanes and trialkylboranes. Ligand exchange between trialkylalanes and trialkylboranes provides another approach to trialkylalanes.[6] This method has its shortcomings: the borane product must be volatile such that it is evaporated away in order to drive the reaction toward completion.

$$Me_3Al + B[CH_2C(Me)CH_2]_3 \rightarrow Me_3B + Al[CH_2C(Me)CH_2]_3 \qquad \textbf{equation 1-5}$$

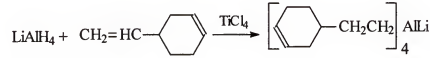
Transmetallation. An alternative method for the synthesis of trialkylalanes involves transmetallation; this method is one of the more versatile ways for preparing trialkylalanes in the laboratory. Reactions of aluminum bromide or chloride with three

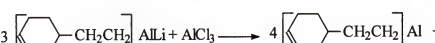
equivalents of an organolithium or Grignard reagents afford the corresponding trialkylalanes (equations 1-6 and 1-7). In the transmetallation process,[7] the more electronegative ligands bind to the more electropositive metal while the less electronegative ligands associate with the less electropositive metal, regardless of the bulkiness of the alkyl groups.

$$3RLi + AlX_3 \rightarrow AlR_3 + 3LiX \qquad \textbf{equation 1-6}$$

$$3RMgX + AlX_3 \rightarrow AlR_3 + 3MgX_2 \qquad \textbf{equation 1-7}$$

Reaction of alkenes with lithium aluminum hydride or dialkylaluminum hydride. Synthesis of trialkylaluminums can be achieved by reacting terminal olefins with either lithium aluminum hydride[8] or dialkylaluminum hydride.[9] Hydroalumination reactions of olefins with the two aluminum reagents mentioned above occur at elevated temperatures and usually follow the anti-Markovnikov orientation (equations 1-8 and 1-9). Either zirconium or titanium tetrachloride is usually employed as a catalyst for the reaction of lithium aluminum hydride with a terminal olefin.





equation 1-8

$$H_2C{=}CHR^1 + R_2AlH \longrightarrow R_2AlCH_2CH_2R^1 \qquad \textbf{equation 1-9}$$

Properties of Organoaluminums

The binary trialkylaluminum compounds are usually colorless liquids that react violently with air and water. Aluminum alkyls with short chain lengths such as trimethyl

or triethylaluminum are pyrophoric. Since they react with water explosively, organoaluminum compounds are handled with extreme care in inert atmospheres (N_2 or Ar). Aluminum alkyls are reactive; they rapidly attack all solvents except alkanes and aromatic hydrocarbons. Trialkylaluminum compounds containing β-branched alkyl groups decompose to dialkylaluminum hydrides and alkenes at about 80 °C. Tri(n-alkyl)aluminum compounds are more stable, with thermal decomposition occurring at higher temperatures (about 120 °C). In contrast, organoaluminum alkoxide ($R_{3-m}Al(OR)_m$) and organoaluminum halides ($R_{3-m}AlX_m$) are considerably less reactive.[10]

Bonding and Structure of Organoaluminums

Monomeric trialkylaluminums are electron deficient species. Unless alkyl groups are bulky, trialkylaluminum compounds in solution have a tendency to form dimeric units in order to obtain octet configurations (Table 1-2, Figures 1-1 and 1-2).[11] There are two hypotheses to explain the observed phenomenon. The Al-C-Al bridge may be described as a two-electron three center (*2e 3c*) bonds, constructed by the overlapping of one C sp^3 orbital with two Al sp^3 orbitals (Figure 1-3). Since the distance of Al-Al in dimeric Al_2Me_6 (260 pm) is significantly shorter than the distance of Al-Al in dimeric Al_2Cl_6 (340 pm), this phenomenon implies a direct Al-Al bond interaction. One hypothesis suggested that there is an Al-Al σ-bond in the dimeric unit of trialkylalanes rather than the two electron three center bond mentioned above. The actual situation may reside between two alternatives.

Table 1-2. Structural features of trialkylalanes.

Substrate	Gas	Solution (non-coordinating solvents)	Solid
Me_3Al	Dimer ↔ monomer	Dimer	dimer
Et_3Al	Monomer	Dimer	dimer
n-Pr_3Al	Monomer	Dimer	dimer
i-Bu_3Al	Monomer	Monomer	dimer
Ph_3Al	Monomer	dimer ↔ monomer	dimer

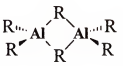


Figure 1-1. R = Me, Et, n-Pr, and Ph

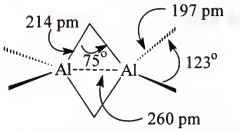


Figure 1-2. Structural data for Me_6Al_2

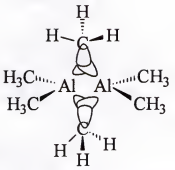
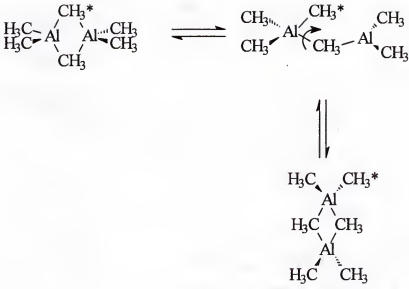


Figure 1-3. (2*e* 3*c*) bonds in $Al_2(CH_3)_6$

Confirmation of the Association of Trialkylaluminum

The dimerization of certain trialkylaluminums is confirmed by ^1H NMR and ^{13}C NMR. At room temperature, trimethylaluminum shows one sharp peak at about 0.3 ppm. As the temperature decreases, the sharp peak starts to resolve into two separate singlets. At about -50 °C, a singlet at 0.5 ppm (bridging CH_3) and another one at -0.65 ppm (terminal CH_3), with relative intensities in a 1:2 ratio, can be observed. The coalescence temperature of the two ^1H NMR signals at -25°C indicates the intramolecular and/or intermolecular exchange of the methyl groups (Scheme 1-2).[11] Alkyl groups are not the only groups which can form bridges; halides, amines, and alkoxides do as well. The relative stability of bridges is listed in Figure 1-4.[11]

Figure 1-4. Relative stability of bridges.
R_2N > RO > Cl > Br > Ph > Me > Et > *i*-Pr > *t*-Bu



Scheme 1-2

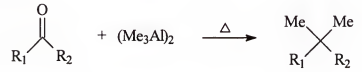
Applications of Aluminum Reagents

Since Ziegler[4] and colleagues discovered the direct synthesis of trialkylalanes and their applications to olefin polymerizations, organoaluminums have become widely accepted in industry and laboratory. Organoaluminums are amphoteric in the sense that the aluminum atom may function as a Lewis acid center, while the anionic alkyl ligands may act as a base (or nucleophile). Capitalizing on this duality, organoaluminum reagents have been widely employed as alkylating reagents, Lewis acids, and reducing agents. Applications of organoalanes in organic synthesis include reactions with unsaturated hydrocarbons, aldehydes and ketones, acid derivatives, alcohols and their derivatives, ethers, epoxides and acetals, halohydrocarbons, nitrogen compounds, and sulfur compounds.[3, 12]

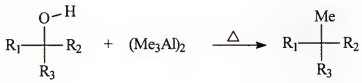
Alkylation

Trialkylalanes are commonly chosen to convert aldehydes to secondary alcohols and ketones to tertiary alcohols by addition. Alkylations normally requires one mole (or more) alane per mole of substrate. Alkylaluminum halides are poor alkylating agents because of their lower reactivity and strong Lewis acidity. Alkylaluminum alkoxides usually act neither as alkylating nor as reducing agent due to aggregation.

In 1970, Mole and his colleagues reported on the ability of trimethylaluminum to act as an exhaustive methylating reagent in its reactions with ketones, tertiary alcohols and benzylic alcohols (Schemes 1-3 and 1-4).[13, 14, 15] Yields from these methylation reactions range from 30% to 100% conversion. Reactions require 2-3 equivalents of trimethylaluminum in a sealed tube under various solvent and temperature conditions as well as reaction times.



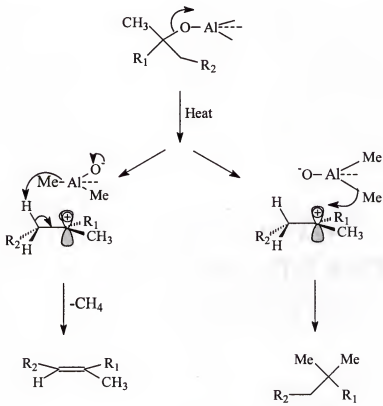
Scheme 1-3



Scheme 1-4

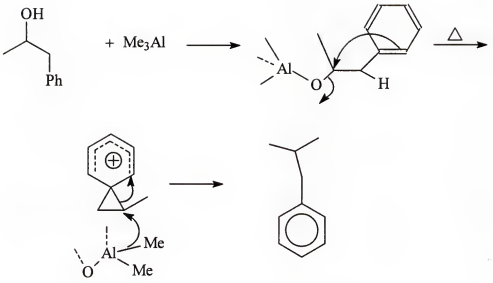
Alkenes occur as the major side products of these methylation reactions with byproduct yields ranging from a small trace up to 50% for some reactions.[15] Accounting for this

observation, Mole concluded that a carbocation was produced prior to methylation, allowing for the possibility of alkene formation. The mechanism is summarized in Scheme 1-5 (note, for simplicity the monomeric form of the alkoxyalane is utilized in the mechanism)

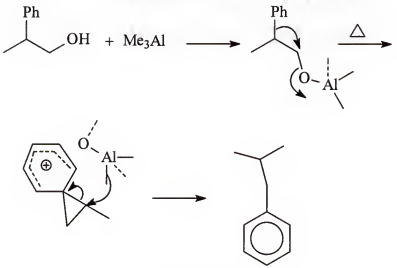


Scheme 1-5

Besides the evidence mentioned above, Mole also discovered a rearrangement reaction when trimethylaluminum reacted with 1-phenylpropan-2-ol. Both reactions of trimethylaluminum with 1-phenylpropan-2-ol and 2-phenylpropan-1-ol afforded isobutylbenzene at about 200 °C (Schemes 1-6 and 1-7). This experimental observation provided strong evidence that the methylation involved carbocations as intermediates.



Scheme 1-6



Scheme 1-7

In their study of the reactions of alcohols with trimethylalane under various conditions, Mole and coworkers discovered that the reactions proceeded more efficiently if small amounts of acetic acid or water were added to the reaction solutions, but are more sluggish if ether or THF were introduced. They suggested that in situ formation of alumoxanes assisted the methylation reactions. We employed alumoxanes in our later investigation of what we refer to as "Organoaluminum Promoted Abnormal Peterson Olefination". These elimination reactions of β-silylalkoxides assisted by alumoxanes afforded either vinylsilanes or allylsilanes with high chemo- or regio-selectivity and from good to moderate yields. These results will be discussed in Chapter 2 and 3.

Alumoxanes

Alumoxanes are species containing an oxygen bridge binding two aluminum compounds. They are produced by the reactions of organoaluminums with water. Since 1960, they have been employed as catalysts in the polymerization of propylene oxides, epoxides, propylene, etc.[16]

Preparation

Direct addition of water to organoaluminums is extremely exothermic and affords decomposition products only (equation 1-10).

$$R_3Al + H_2O \rightarrow Al(OH)_3 + 3RH \qquad \textbf{equation 1-10}$$

Several methods for the preparation of alumoxanes were discussed in Pasynkiewicz's review.[16] One of the methods discovered by Saegusa is to control the hydrolysis of triethylalanes by slowly adding a precise amount of deionized water (equation 1-11).[17]

$$Et_3Al + 3\ H_2O \rightarrow Et_2AlOH + EtH$$

$$Et_2\ AlOH + Et_3Al \rightarrow Et_2AlOAlEt_2 + EtH$$

$$Et_2AlOAlEt_2 + H_2O \rightarrow Et_2AlOAl(Et)OH + EtH \quad \textbf{equation 1-11}$$

Reactions of trialkylalanes with copper sulfate pentahydrate in aromatic hydrocarbon medium were described by Razuvaev[18] (equation 1-12). It is now commonly employed in alumoxane synthesis.

$$8\ AlR_3 + CuSO_4{\cdot}5H_2O \rightarrow 4\ R_2AlOAlR_2 + CuSO_4{\cdot}H_2O + 8\ RH \quad \textbf{equation 1-12}$$

A method producing alumoxanes without formation of gaseous products was disclosed by Araki[19] and co-workers. It involved reactions of equimolar quantities of R_2AlOLi with R_2AlCl in toluene at -20 °C (equation 1-13).

$$R_2AlOLi + R_2AlCl \rightarrow R_2AlOAlR_2 + LiCl \quad \textbf{equation 1-13}$$

Mechanism

Since small alkyl containing alumoxanes exhibit rapid exchange reactions and the presence of multiple equilibria, crystallographic data have been obtained for only a few alumoxanes. Crystallographic data are available for the alumoxanes which contain bulky ligands and are ionic. However, Boleslawski and Serwatowski have proposed a mechanism for the controlled hydrolysis of alanes by monitoring the reaction course using ^1H NMR spectroscopy (Scheme 1-11).[20]

$$AlR_3 + H_2O \rightarrow R_3AlOH_2$$

$$R_3AlOH_2 \rightarrow R_2AlOH + RH$$

$$mR_2AlOH \rightarrow (R_2AlOH)_m$$

$$(R_2AlOH)_m \rightarrow (RAlO)_m + mRH$$

R = Me, Et, *i*-Bu.

Scheme 1-11

Historical Background and Properties of Silicon

In the earth crust, the second most abundant element is silicon. Silicon is characterized as a semimetal and it exists in two allotropic forms: a dark brown, powdery amorphous form and gray, metallic-like crystalline form. It was isolated and characterized in 1824 by Jöns Jacob Berzelius. A group IV semi-metal (Table 1-4), silicon has isotopes with atomic weights between 24 and 34; silicon-28 is 92.23 % naturally abundant.[21]

Table 1-4. Properties of Silicon.

Element	Silicon
Electron Configuration	Ne $3s^2 3p^2$
Atomic number	14
Atomic weight	28.0855
Melting point	1410 °C
Boiling point	2355 °C
Oxidation state	+ 2, + 4, - 4
Specific Gravity	2.33 @ 25 °C

Production of silicon and its derivatives

Crystalline silicon (96-98 % pure) can be made by reacting SiO_2 with carbon in an electric furnace, followed by zone refining. An alternative method involves reaction of sodium fluorosilicate with sodium to first produce silicon tetrafluoride that further reacts with sodium to produce silicon in high purity.[22]

Halosilanes

In organosilicon chemistry, chlorosilanes are widely employed as starting materials. Tetrachlorosilane can be obtained either from the reaction of silicon and chlorine or from heating silicon dioxide, coke and chlorine together.[23] Why is tetrachlorosilane a useful starting material? It is because the chloride of the silane can be easily replaced one at a time by a variety of nucleophiles to produce compounds like dimethylphenylchlorosilane, diphenylmethylchlorosilane and triphenylchlorosilane. The

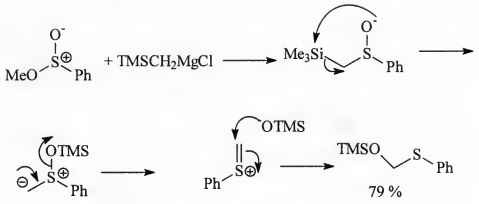
reactivity of chlorosilanes decrease as the number of alkyl groups increase, therefore, it is usually easy to replace the chlorides one at a time (Scheme 1-12).[24]

Scheme 1-12

Properties of Organosilicons

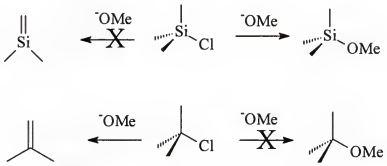
Although silicon and carbon are both group IV elements, their reactivities are quite different from each other. Some of the differences between these analogs may be due to the presence of d-orbitals in silicon, but not in carbon. Fleming[24] divided organosilicon chemistry into eight categories. Six of them are listed below:

Chlorine, fluorine, and oxygen silicon single bonds are very strong. Silicon has strong affinity for chlorine, fluorine, and oxygen. The strong single bonds of silicon with these elements normally govern reaction outcomes. In a reaction, formation of a Si-O, Si-Cl, or Si-F bond is preferred at the expense of a weaker bond such as Si-C, Si-H or Si-N bond (Scheme 1-13).



Scheme 1-13

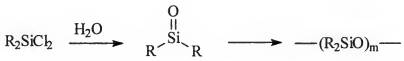
Nucleophilic attack at silicon is relatively easier than the corresponding nucleophilic attack at carbon. It is rather difficult to displace C-H, C-F and C-OR with nucleophiles. Surprisingly, nucleophilic substitution at silicon is much easier, even a poor leaving group can be replaced. Thus, Si-H, Si-C, Si-OR, and Si-F bonds are capable of being replaced by Si-Nu bonds as long as suitable nucleophiles are chosen (Scheme 1-14).



Scheme 1-14

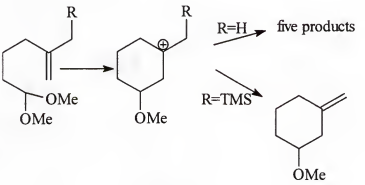
Silicon double bonds are weak. Carbon can form a double bond with oxygen to make a ketone, but the silicon equivalent of a ketone is unstable. For example, hydrolysis of dichlorodimethylsilane gives oligomers or polymers instead of silanone. The reason may

due to the disparity in size between silicon (third row element) and elements like carbon and oxygen (second row element). In general, silicon π bonds are weak.



Scheme 1-15

Nucleophilic attack at silicon is much faster than either at carbon or at hydrogen if oxygen or halogens are nucleophiles. Fleming[25] reported on the reaction of the acetals (R = H and $SiMe_3$, Scheme 1-16) with formic acid. These reactions first produce carbocations as intermediates. In the case of acetal without the TMS substituent (R = H), reaction gave five products: two diastereoisomeric ethers and three possible olefins. By contrast, reaction of the acetal containing the TMS group (R = TMS) gave one olefin product in which the double is installed by the loss of the TMS substituent. This phenomenon suggested nucleophilic attack at silicon is much faster than at either carbon or hydrogen if oxygen or halogens are nucleophiles.



Scheme 1-16

Silicon stabilizes adjacent carbanion. In spite of its electron donating nature, silicon is capable of stabilizing an α-carbanion. The most popular reason given is the conjugation of the carbanion with silicon empty d-orbitals. Examples demonstrating how silyl groups stabilize adjacent anions include: the observation that silanols are more acidic than water, triphenylsilylthiol is almost as strong an acid as acetic acid, and silylamines are generally less basic than simple amine.

Silicon-carbon bond stabilizes β carbocation. A silicon-carbon bond can stabilize a carbocation through hyperconjugation (Figure 1-5). The overlap of Si-C σ-bond with an empty p-orbital at an adjacent carbocation site results in energy lowering and stabilization of the electron deficient species. The hyperconjugation from Si-C bond is usually referred to as the β–silyl effect. The first observed evidence for this effect was from the relatively fast protodesilylation of silylbenzene compare to the methyl analog. [26,27]

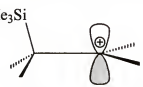


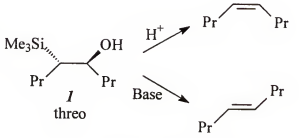
Figure 1-5

Peterson Olefination Reaction

Elimination of β-silylalkoxide anions to give an alkene was first discovered in 1947.[28] In 1968, Peterson[29] described the preparation of functionalized alkenes from α-silyl carbanions and has done intensive study on this olefination reaction in both acidic and basic media.

The Peterson olefination reagent ($(CH_3)_3SiCH_2M$, M = Li, MgX) reacts with aldehydes, and ketones thus affording the corresponding β-hydroxysilanes. A unique property of this Peterson olefination reagent is the stabilization of the organometallic reagent provided by the silyl group and in the direct elimination of the hydroxyl group in the product alcohol. The silyl group stabilizes the α-anion in the Peterson olefination reagent and it also assists the removal of the hydroxyl group in elimination under acidic conditions via an E2 like elimination (β-silyl effect[30]) and under basic condition via a syn elimination.

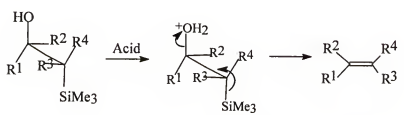
The stereospecificity of the elimination was not known until 1974.[31] Hudrlik and Peterson synthesized highly pure threo diastereomer of 5-trimethylsilyl-4-octanol ***I*** and reacted it with acid and base. Reaction of ***I*** with acid afforded cis-4-octene, while reaction of ***I*** with base produced trans-4-octene (Scheme 1-16).



Scheme 1-16

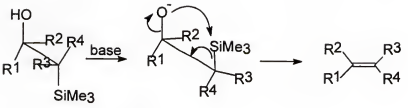
When alkyl, hydrogen, or electron-donating substituents are present on the carbon atom bonded to silicon, β-hydroxysilanes can be isolated. Therefore, the stereochemical outcome of the Peterson olefination reaction can be governed by the choice of conditions.

When electron-withdrawing substituents are present on the carbon atom bonded to silicon, reactions of the Peterson olefination reagents with aldehydes or ketones give the alkene directly with poor isomeric purity and isolation of β-hydroxysilanes are usually not possible. The exact mechanism of the Peterson olefination is still unclear. No direct experimental evidence has been obtained to support the proposed mechanisms; however, they were proposed based on the stereochemistry of the products under acidic or basic conditions. It has been suggested that elimination under acidic conditions occurs through an E_2 like anti-periplanar transition state (Scheme 1-17).

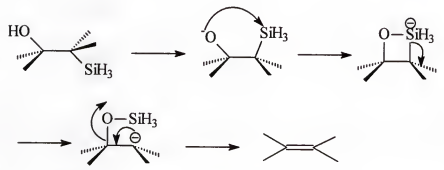


Scheme 1-17

Two mechanisms were suggested for the base promoted elimination. The generally accepted mechanism involves a syn-periplanar transition state (Scheme 1-18).[31] Carey, Hwang and Trindle[32] suggested another possible mechanism involving an E_{1cb} like stepwise pathway (Scheme 1-19). They employed CNDO calculations to study the elimination pathway. The result suggested that the stepwise pathway, involving silicon-carbon bond cleavage, was more favorable than the concerted elimination.

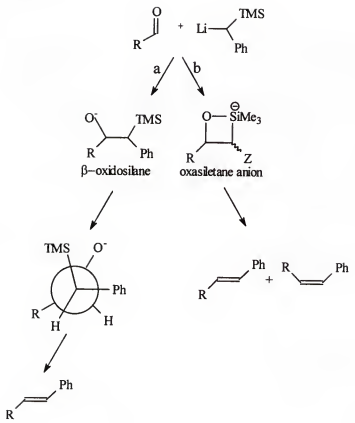


Scheme 1-18



Scheme 1-19

Among several postulated mechanisms, one involving initial C-C bond formation which leads to a β-oxidosilane intermediate (path a) and should give products to high isomeric purity. Since the stereo-outcomes in some reactions are poor, path a is unlikely be the major pathway for Peterson olefination in basic condition. Hudrlik[33] proposed the possibility that C-C bond formation and Si-O bond formation may be concerted to form oxasiletane anion directly (path b). Thus, reactions may yield an olefin with poor isomeric selectivity (Scheme 1-20).


O
R
+
Li
TMS
Ph
a
b
O⁻
TMS
R
Ph
β–oxidosilane
O
SiMe3
R
Z
oxasiletane anion
TMS
O⁻
Ph
R
H
H
Ph
R
Ph
+
R
Ph
R

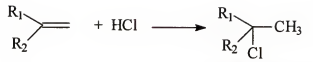
Scheme 1-20

CHAPTER 2
TRANSFORMATION OF KETONES TO VINYLSILANES

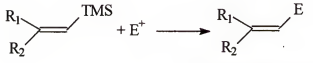
Vinylsilanes

When alkenes react with electrophiles, reactions usually give addition products that follow Markovnikov orientation.[34] Unlike alkenes, vinylsilanes usually react with electrophiles to give substitution products; silyl groups are normally replaced by electrophiles and double bonds remain intact (Scheme 2-1). As mentioned in Chapter 1, nucleophilic attack at silicon is relatively easier than the corresponding nucleophilic attack at carbon; therefore, substitutions are favored over additions in the electrophilic reactions of vinylsilanes. Although Markovnikov's rule does not apply in the electrophilic substitution of vinylsilanes, vinylsilanes react with electrophiles in regio- and stereo-selective manners. In the case of substitution, the site of the silyl group in the starting material normally determines both the site of attack and the site of the double bond in the product.

Historically, the first electrophilic substitution of a vinylsilanes was carried out in 1954[35] and the first electrophilic substitution of a vinylsilane using a heteroatom was sulfonation in the late 1960s.[36] Regioselectivity and stereoselectivity of the electrophilic substitution of vinylsilanes were reported in the early 1970s. These aspects will be discussed in detail in a later chapter.[37,38]



addition product

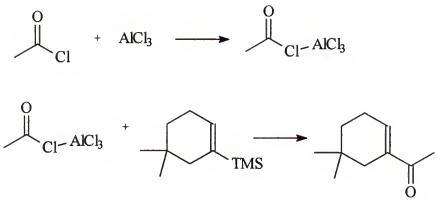


substitution product

Scheme 2-1

Formation of Unsaturated Carbocycles via Vinylsilanes

Vinylsilanes are valuable intermediates in natural product synthesis because they function as vinyl anion equivalents in electrophilic reactions. These reactions have been successfully conducted under a variety of conditions. Bimolecular Friedel-Crafts acylation of vinylsilanes has been studied for more than 30 years (Scheme 2-2).[38] The first intramolecular vinylsilane-terminated cyclization was reported by Burke in 1981 for the synthesis of spiro[4.5]decadienones (Scheme 2-3).[39]

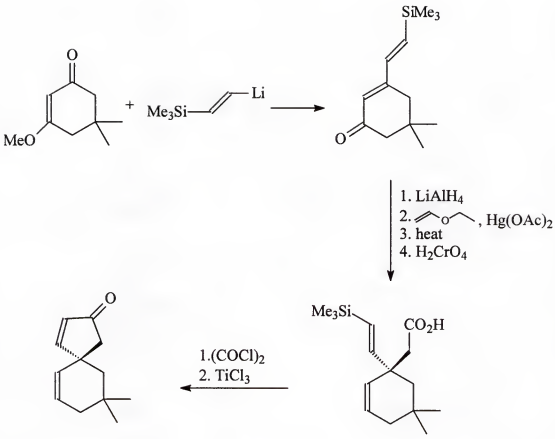


Scheme 2-2

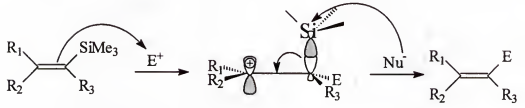
Regioselectivity

In general, the electrophilic substitution of vinylsilanes is regioselective (Scheme 2-4). Electrophiles attach to the olefinic carbon bonded to the silyl group, followed by removal of the silyl groups.[39] Since the loss of a silyl group is faster with oxygen or halogen nucleophiles than is the loss of a proton,[40] the atom to which the silicon is attached determines the final position of the double bond.

Regioselectivity is governed by the β-silyl effect in which cation intermediates are stabilized by hyperconjugative overlap of the Si-C bonding orbital with the empty p-orbital.[27, 41] The β-silyl stabilization of a carbocation is calculated to be 38 kcal mol^{-1} greater than the ethyl cation.[42] However, the site of the electrophilic attack does not always lead directly to the β-silyl stabilized cation. Even if it does, the silyl group is not quite always the electrofugal group.[43] Since the goal of this dissertation is to report a development of a new methodology in making allyl- and vinyl- silanes, the regioselectivity problem is not discussed in great detail.



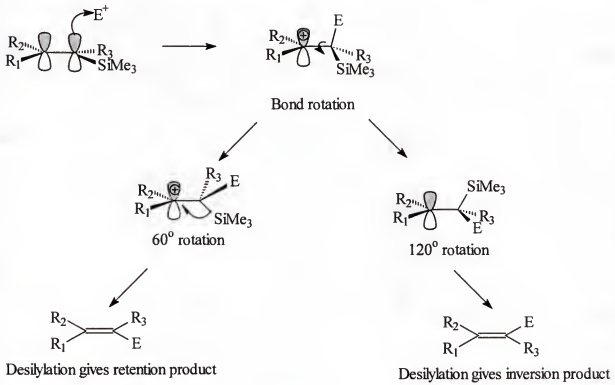
Scheme 2-3



Scheme 2-4

Stereoselectivity

Electrophilic substitution of vinylsilanes is not only regioselective but also stereoselective. The reaction can give a product with either retention or inversion of configuration. The stereo-outcome is determined by the degree of bond rotation of the silyl group. As shown in Scheme 2-5, the initial attack takes place on the carbon bonded to silyl group. The silyl group rotates into position to stabilize the carbocation.[44] If the silyl group rotates 60° followed by desilylation, a retention product is produced. If the silyl group rotates 120° in an opposite direction followed by desilylation, an inversion product is produced. Substitution reactions typically involve minimal rotation, therefore, the product which exhibits retention of configuration usually dominates.



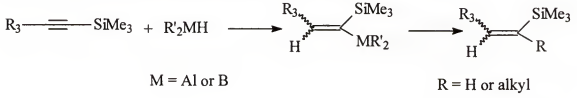
Scheme 2-5

Synthesis of Vinylsilanes

The applications of vinylsilanes to organic synthesis previously presented demonstrate their usefulness as reagents. There are several methods available for the preparation of vinylsilanes. These generally involve transformations of alkynes, aldehydes and ketones to vinylsilanes adducts, each of which will be discussed in the following sections.

Transformation of alkynes to vinylsilanes

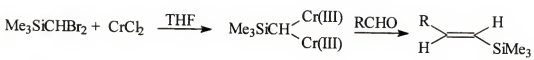
The most popular literature method involves reduction of alkynylsilanes to the corresponding vinylsilane anions. Further alkylations of the vinylsilane anions afford the desired products.[45,46] The general method is summarized in Scheme 2-6.



Scheme 2-6

Transformation of aldehydes to vinylsilanes

Takai and his coworkers reported a stereoselective synthesis of *E*-vinylsilanes from aldehydes.[47] In this methodology, aldehydes are reacted with a proposed gem-dichromium reagent prepared by $CrCl_2$ reduction of $Me_3SiCHBr_2$ in THF to produce the corresponding vinylsilanes (Scheme 2-7).



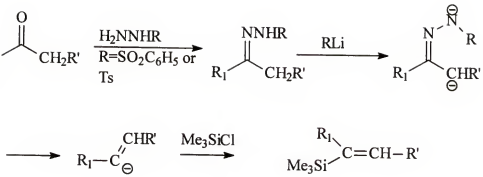
E/Z = > 90/ <10

Scheme 2-7

Transformation of Ketones to Vinylsilanes

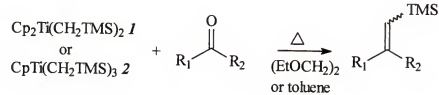
There are several general methods to convert ketones to vinylsilanes reported in the literature. One method employs the Shapiro reaction to convert ketones to vinyldiimides and thence to the vinyl anions, then further reacting the vinyl anions with TMSCl to produce the corresponding vinylsilanes. A second method involves conversion of ketones to vinylsilane phosphates. Reaction of the vinylsilane phosphates with dialkyl cuprates then affords the desired vinylsilanes. A third method involves reactions of dithioacetals or dithioketals with trimethylsilylmethylmagnesnium halides in the presence of nickel (II) catalysts to produce vinylsilane adducts. A fourth method involves the Peterson olefination reaction of the β-disilylalkoxide anion intermediate to make mono-silylated vinylsilanes.

Application of the Shapiro reaction in vinylsilane synthesis. The Shapiro reaction[48,49] can be employed to make vinylsilanes. In this process, ketones are first converted to their corresponding vinyldiimides at – 78 °C. On warming nitrogen is evolved and the resulting vinyl anions are treated with trimethylsilylchloride to produce the desired vinylsilanes in reportedly fair to good yields (Scheme 2-8). Note that this method does not alter the carbon skeleton.



Scheme 2-8a

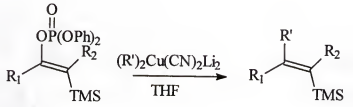
Titanium-mediated carbonyl olefinations. A preparation of one carbon elongated vinylsilanes, has been developed by Petasis[50] which utilizes the reactions of bis(trimethylsilylmethyl titanocene derivative ***1*** or cyclopentadienyl tris(trimethylsilylmethyl) titanium (IV) ***2*** with carbonyl derivatives. The reaction works with aldehydes, ketones, and ester afford vinylsilanes in fair to good yield, but with low *E/Z* stereoselectivity (Scheme 2-8b).



Scheme 2-8b

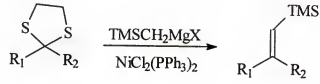
Conversion of vinylsilane phosphates to vinylsilanes. Koerwitz and coworkers[51] disclosed a vinylsilane synthetic method by first converting ketones to vinylsilane phosphates (***VSP***), and then reacting the ***VSP*** with alkyl cuprates to produce vinylsilanes in poor to good yield (Scheme 2-9). This method suffers from the requirement of

preparing the moderately stable α-silyl ketone starting material. Also, it is not suitable for diarylketones.



Scheme 2-9

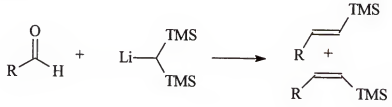
Nickel catalyzed silylolefination of dithioacetals. A method involving conversion of dithioacetals and dithioketals to vinylsilanes was disclosed recently by Ni and coworkers.[52] Aldehydes or ketones are first transformed to dithioacetals and dithioketals, which are then reacted with the appropriate Grignard reagents in the presence of a Ni(II) catalysts to produce a one carbon elongated vinylsilane in fair to good yields (56 – 91 %) (Scheme 2-10). This method is most similar to our procedure described below; however, it requires preparation of the dithioacetal or ketal in a preliminary step.



Scheme 2-10

Reactions of carbonyl compounds with [bis(trimethylsilyl)methyl]lithium. In 1974 Gröbel and Seebach[53] reported a method to make vinylsilanes which involved the reaction of carbonyl compounds with [bis(trimethylsilyl)methyl]lithium in THF / HMPA to give a mixture of trans- and cis-vinylsilanes (Scheme 2-11).

Bis(trimethylsilyl)methyllithium is usually generated by reacting bis(trimethylsilyl)methane with t-butyllithium at temperatures between -90 to -78 °C for 10 hours prior to use. Reaction of bis(trimethylsilyl)methyllithium with the carbonyl compound gives a β-bissilylalkoxide anion intermediate which undergoes a Peterson-type elimination of $TMSO^-$ to give the mono-silylated vinylsilane. The mechanism is believed to proceed by means of an oxasiletane anion mentioned in chapter one, therefore, the isomeric selectivity is poor.



Scheme 2-11

Application of Organoaluminums in Vinylsilanes Synthesis

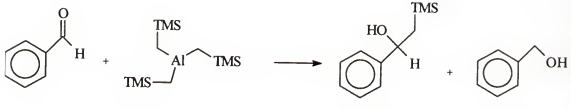
Synthesis and Development of a Selective Peterson Olefination Reagent: Tris(trimethylsilylmethyl)aluminum lithium bromide Complex *2-1*.

The main goal of this dissertation is to report the development of a modification of the Peterson olefination.[29] As mentioned in chapter 1, organoaluminums have been widely employed in alkylation and reduction of organic compounds. In 1970, Beachley reported a method which involves a twelve hour reflux of a 3 : 1 mixture of trimethylsilylmethyl lithium and aluminum bromide in hexanes to produce a white paste: tris(trimethylsilylmethyl)aluminum lithium bromide complex ***2-1*** (equation 2-1).[54]

$3\ TMSCH_2Li + AlBr_3 \rightarrow (TMSCH_2)_3Al{\bullet}3LiBr \rightarrow (TMSCH_2)_3Al$ **equation 2-1**

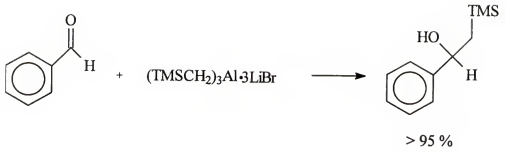
2-1 distillation ***2-2***

The distillation of tris(trimethylsilylmethyl)aluminum ***2-2*** from ***2-1*** started at 70 °C and a pressure of 0.1 mm Hg, affording the product in 56 % yield. One of the previous projects from our group was to explore the reactivity of the silylated alanes as selective Peterson olefination reagents.[55] Reactions of ***2-2*** with aldehydes gave addition and reduction products in various ratios. For example, reaction of ***2-2*** with benzaldehyde gave 53 % yield of the addition product and 27 % yield of reduction product (Scheme 2-12).

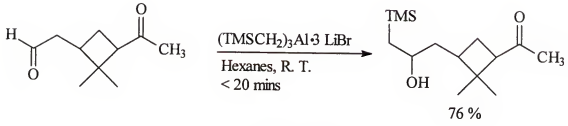


Scheme 2-12

Since the results from distillations of ***2-2*** and reactions with carbonyl compounds were not satisfactory and colorless tris(trimethylsilylmethyl)alane ***2-2*** is pyrophoric, reactivity of the relatively stable salt [tris(trimethylsilylmethyl)aluminum, LiBr ***2-1***] was examined. Experimental results indicated the potential of ***2-1*** as a selective Peterson olefination reagent. Reaction of ***2-1*** with aldehydes at room temperature afforded mainly addition products. For example, reaction of ***2-1*** with benzaldehyde afforded only the addition product (Scheme 2-13). The non-pyrophoric tris(trimethylsilylmethyl)aluminum lithium bromide salt ***2-1*** not only facilitates a cleaner reaction, but also selectively reacts with aldehydes over ketones (Scheme 2-14).



Scheme 2-13



Scheme 2-14

My work began by exploring the reaction of tris(trimethylsilylmethyl)aluminum lithium bromide salt ***2-1*** with ketones at elevated temperature, which led us to the current direction of study. We anticipated the outcome of these reactions to be the normal Peterson olefination products. Surprisingly, reaction of ***2-1*** with benzophenone afforded mainly the vinylsilane. This result posed an interesting mechanistic problem with considerable synthetic merit. Unfortunately, results from the reaction of ***2-1*** with ketones other than diaryl types were not satisfactory for reasons that remain to be clarified. Since the formation of vinylsilane from the reaction of ***2-1*** with benzophenone involves an addition step followed by elimination of an aluminate group, it was reasonable to conclude that the problem lay in the relatively slow addition step with reagent ***2-1***. To avoid the problem of addition of the trimethylsilylmethyl group to the ketone, we decided

to use the more reactive trimethylsilylmethyllithium. Subsequent addition of a dialkylchloroalane could be employed to form the dialkylaluminate required for the elimination step to produce the desired products, namely one carbon elongated vinylsilanes. Thus one would have a "one-pot" reaction protocol to proceed directly from ketone to vinylsilane, a process not dissimilar from the Wittig reaction.

Preliminary Investigation

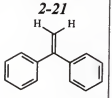
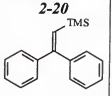
At the beginning of our investigation, we reacted diethylchloroalane or trimethylalane with alkoxides or alcohols, respectively, at reflux under different reaction conditions to explore the feasibility of this methodology. Analysis of the crude reaction products was accomplished by ^{1}H NMR using anisole as an internal standard for determination of yields.

Reactions of benzophenone. The alkoxide anion of benzophenone was generated by reacting benzophenone with 1.2 equivalents of trimethylsilylmethyllithium (in hexanes) at 0 °C. To the alkoxide anion solution, 1.4 equivalents of diethylaluminum chloride were added, followed by refluxing overnight. After workup, in addition to the recovered starting material, the main product was 1,1-diphenylethene ***2-21*** (39%) with (2,2-diphenylvinyl)trimethylsilane ***2-20*** (10%) as the minor product.

Reactions with 1,1-diphenyl-2-trimethylsilylethanol *2-19*. In addition to the above benzophenone reaction, 1,1-diphenyl-2-trimethylsilylmethylethanol ***2-19*** was synthesized and reacted with two different concentrations of trimethylalane. Reaction of ***2-19*** with trimethylalane should proceed analogously to the reaction described in previous section. Therefore, we should gain insight into the mechanism in the elimination process. The

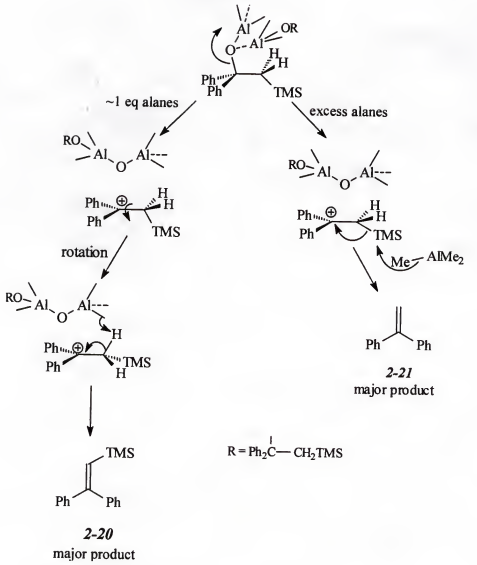
results for the reaction of ***2-19*** with trimethylalane affording ***2-20*** and ***2-21*** are summarized in Table 2-1.

Table 2-1. Results of reactions of ***2-19*** with Me_3Al.

No. of eq. of trimethylalanes used	Solvent	Hours of reflux	% yield of ***2-21*** 	% yield of ***2-20*** 
1.1	Hexanes	15	37	62
3.1	Benzene	3	67	14`

It is striking that increasing the number of equivalents of trimethylalane decreased the proportion of the vinylsilane. To explain these results, a mechanism was proposed as shown in Scheme 2-15. (Note: The carbocationic nature of this reaction is supported by evidence given later in this chapter.)

In this E1-like elimination process, the carbon-silicon bond is weakened by hyperconjugation. Therefore, the silyl group should be more readily removed by a nucleophile. When approximately 1 equivalent of alane was used for conversion of the alcohol to the alkoxyalane intermediate, aggregate organoaluminums are likely to form in the reaction mixture. The aggregation around the aluminum complexes is likely to force the aluminum complexes and the silyl groups to remain in an anti-periplanar relationship. Since there is no large excess of the less hindered trimethylalanes available to attack the silyl group, proton abstraction occurs from the face opposite of the TMS group. Therefore, vinylsilane ***2-20*** is the major product of the reaction.


~1 eq alanes
excess alanes
rotation
TMS
Ph
Ph
H
OR
RO
Al
O
Me
AlMe2
R = Ph2C— CH2TMS
2-21
major product
2-20
major product

Scheme 2-15

The concentration of oligomeric organoaluminums, including alumoxanes $(RAlO)_n$ increases as the elimination process proceeds, but in the presence of an excess trimethylalane, the silyl group may be intermolecularly abstracted by the alane yielding diphenylethylene as the major product. As mentioned in chapter one, alkyl groups on an aluminum that are not bonded to a heteroatom are more basic and/or nucleophilic than similar alkyls on an aluminum bonded to a heteroatom. This argument may explain the product distributions of these reactions with various amounts of trimethylalane; however, the chemoselectivity is not satisfactory, so a modification was developed to improve the product distribution and increase the yield of the vinylsilane.

Based on preliminary result from the reaction of tris(trimethylsilylmethyl)aluminum lithium bromide complex with benzophenone,we realized high chemoselectivity was attainable. As an undergraduate organic student is taught, a reaction outcome is normally governed by electronic factors, steric factors, or a combination of both. In our case, I believe it is the combination of both which governs our reaction outcome. Since an organoaluminum is extremely oxophilic, in our early modification of the "Abnormal Peterson Olefination," we introduced ether to the system to increase the bulkiness of the alanes. Experimental data indicated the chemoselectivity was improved dramatically, but the yield of the desired TMS adducts was low. This may be due to lowering of the reflux temperature caused by ether. The details of these investigations will be discussed in Chapter 3.

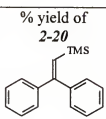
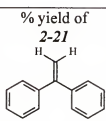
Organoaluminum Promoted "Abnormal Peterson Olefination"

After a series of examinations, it appeared that increasing the aggregation (bulkiness) of the base (alane) improved the chemoselectivity of the "Abnormal Peterson Olefination" to produce mainly the vinylsilane. Moreover, as the reaction proceeds, alkyl groups on the organoaluminum derivatives decrease its nucleophilicity and basicity due to increasing oxygen substitution on aluminum. Thus, the trimethylsilyl group would be less susceptible to elimination during the course of the reaction. We employed GC to monitor the reflux reaction of 1,1-diphenyl-2-trimethylsilylethoxide anion with 1.4 equivalents of diethylaluminum chloride. Olefin product dominated initially, but remained nearly constant throughout the reminder of the reaction, while the amount of vinylsilane increased as reaction proceeded. Therefore, we investigated ways to determine the requirement for the system.

Roesky[56] reported a study of the controlled hydrolysis of alanes to produce alumoxanes. We employed this method to create a catalytic amount of alumoxanes, in situ, prior to the elimination process. Thus, benzophenone was first reacted with 1.2 equivalents of trimethylsilylmethyllithium to produce the corresponding alkoxide at 0 °C. To the alkoxide solution, 1.4 equivalents of diethylaluminum chloride was added, followed by the introduction of small amounts of distilled water in THF at 0 °C. The resulting mixture was allowed to reflux in xylene for 21-43 hours. Under these conditions, the organoaluminum promoted "Abnormal Peterson Olefination" afforded mainly vinylsilane adduct ***2-20*** in good yield and chemoselectivity. The results are summarized in Table 2-2. Presumably, a catalytic amount of alumoxane is initially

generated by the addition of water and aggregates with the other organoalanes species there by increasing the bulk of the alanyloxide leaving group. Since the structure of these highly aggregated alane intermediates would be difficult to surmise and cogently present a simplified mechanism is proposed to explain our observations (Scheme 2-16). Note that the dashed line to each aluminum atom indicates aggregation to an alumoxane; presumably [EtAlO]. Also, since an equivalent of lithium chloride is generated in the early stages of the one pot reaction we assume it also plays a part in the reaction pathway. Attention should be drawn to the important role played by the trimethylsilyl group in promoting ionization through a stereoelectronically preferred anti-periplanar conformation. Further support for this ionic pathway will be forthcoming.

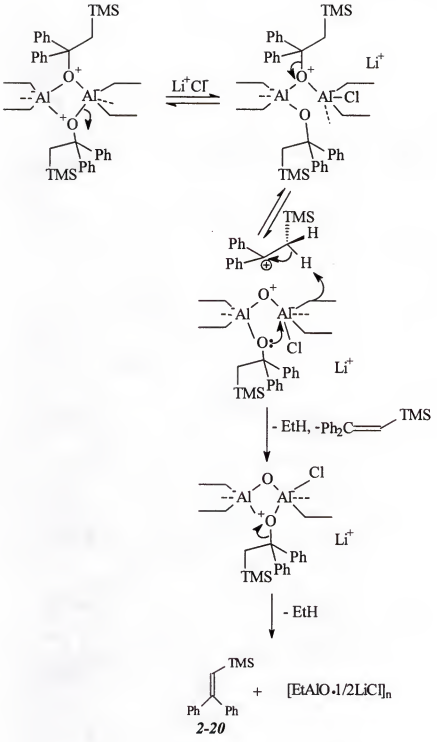
Table 2-2. Organoaluminum promoted "Abnormal Peterson Olefination" with benzophenone[a] under various conditions.

Solvent	No. of eq. of H_2O in THF used	Reflux time (hours)	% yield of ***2-20*** 	% yield of ***2-21*** 
60 mL THF	0.1	26	41	5
50 mL toluene	0.1	43	71	4
27 mL xylene	0.1	24	71	2
27 mL xylene	0.2	24	67	4
27 mL xylene	0.0	21	47	20

[a]benzophenone (0.5 g, 2.7 mmol) was in each reaction.

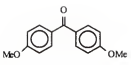
The results in Table 2.2 suggest that alumoxanes are critical for chemoselectivity of the elimination process. It also suggests that 0.1 equivalent of H_2O is sufficient to produce enough alumoxanes in the early stages of the reaction to suppress the formation of the normal Peterson olefination product ***2-21*** and promote the chemoselective elimination. In

fact, we have investigated the method thoroughly by varying the amounts of each of the chemicals employed. Our results indicated that 1.2 eq. of $LiCH_2TMS$, 1.4 eq. of Et_2AlCl, and 0.1 eq. of H_2O in THF afforded the desired product in highest yield and with the greatest chemoselectivity. Therefore, we have employed these conditions to carry on our investigation, with other non-enolizable ketones the results of which are summarized in Table 2-3. Substrates and possible products are listed in Figure 2-1.



2-20

Scheme 2-16



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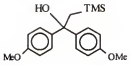
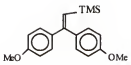


2-7



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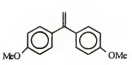

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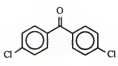

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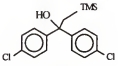
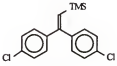
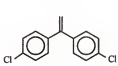


2-11



2-12



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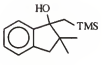

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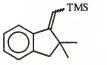

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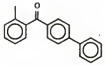
2-26

2-27

2-28

2-29



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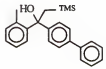
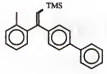
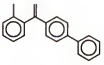


2-31



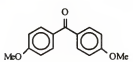
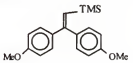
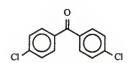
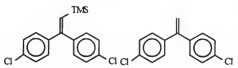
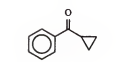
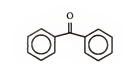
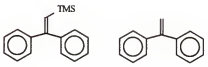
2-32



2-33

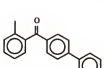
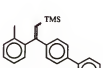
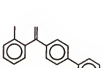
Figure 2-1

Table 2-3. Organoaluminum Promoted "Abnormal Peterson Olefination" in the synthesis of vinylsilanes.

Substrate[a]	Reflux time (hr)	Yield (isolated yields, unless otherwise noted)	Product distribution[c]
	24	83	
2-6			***2-8***
	22	79	
2-10			***2-12*** 19 : ***2-13*** 1
	27	79[b]	
2-14			***2-16*** *(E:Z=1:19)* 78 : ***2-17*** 1
	24	66	
2-18			***2-20*** 10 : ***2-21*** 1

[a] all substrates have a concentration of 0.1 M in xylene.
[b] % yields of the products are determined by ^{1}H NMR with known amount of anisole as internal standard.
[c] product ratios are determined by ^{1}H NMR; each reaction afford $\leq$. 3 % yield of the corresponding olefin.

Table 2-3. Organoaluminums Promoted "Abnormal Peterson Olefination" in the synthesis of vinylsilanes.

Substrate[a]	Reflux time (hr)	Yield (isolated yields, unless otherwise noted)	Product distribution[c]
 ***2-22***	24	61	 ***2-24*** (*E:Z=1:50*)
 ***2-26***	24	76	 ***2-28*** 6 :  ***2-29*** 1
 ***2-30***	27	85[b]	 ***2-32*** (*E:Z=2:1*) 11 :  ***2-33*** 1

[a] all substrates have a concentration of 0.1 M in xylene.
[b] % yields of the products are determined by ^{1}H NMR with known amount of anisole as internal standard.
[c] product ratios are determined by ^{1}H NMR; each reaction afford ≤ 3% yield of the corresponding olefin.

Reactions of phenyl cyclopropyl ketone ***2-14***, 2,2-dimethyl-1-indanone ***2-22***, and 4-phenyl-2'-methylbenzophenone ***2-30*** afforded mixtures of *E/Z* vinylsilane isomers. NOE experiments and ^{1}H NMR were performed on these mixtures to determine the stereochemistry of the major isomers.

In the mixture of 2-phenyl-2-cyclopropylvinyltrimethylsilane ***2-16*** obtained from ketone ***2-12***, irradiation at 5.56 ppm (major vinyl proton) enhanced the signal at 1.68 ppm (cyclopropyl α–protons) by 4 %, indicating the major isomer was (*Z*)-2-phenyl-2-cyclopropylvinyltrimethylsilane (Figure 2-2) . The yield of the major isomer was determined to be 74 % and the minor isomer was 4 % (by ^{1}H NMR with internal standard).

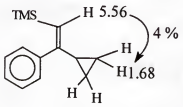
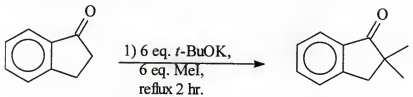


Figure 2-2

2,2-Dimethyl-1-indanone ***2-22***[57] was prepared by dimethylation of 1-indanone. 1-Indanone was reacted with 6 equivalents of potassium *tert*-butoxide and 6 equivalents of methyl iodide at reflux to afford ***2-22*** in 54 % yield (Scheme 2-17).



Scheme 2-17

In the mixture of 1-(1-trimethylsilylmethylidene)-2,2-dimethyl-3,3-dihydro-1*H*-indene ***2-24***, irradiation at 5.56 ppm (major vinyl proton) enhanced the signal at 1.25 ppm (methyl protons) by 3 %, indicating the major isomer was of (*Z*)-1-(1-trimethylsilylmethylidene)-2,2-dimethyl-3,3-dihydro-1*H*-indene (Figure 2-3). The isolated yield of the major isomer was determined to be 60 % and the minor isomer was 1 %.

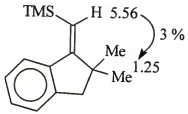


Figure 2-3

In the mixture of [2-(4-biphenyl)-2-(o-tolyl)vinyl]trimethylsilane ***2-32***, irradiation at 2.23 ppm (major methyl signal) enhanced the signal at 5.84 ppm (major vinyl proton) by 5 % which secured the assignment of the major isomer as (*E*)- [2-(4-biphenyl)-2-(o-tolyl)vinyl]trimethylsilane (Figure 2-4). The yield of the major isomer was determined to be 52 % and the minor was 26 %.

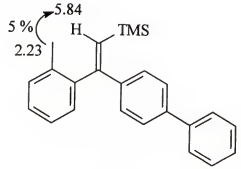
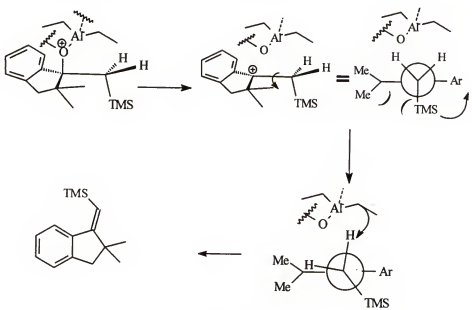


Figure 2-4

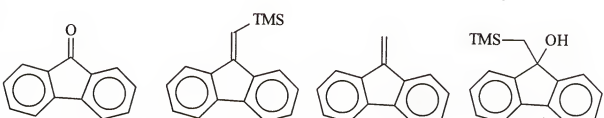
Based on the results listed above, organoaluminum promoted "Abnormal Peterson Olefination" affords vinylsilanes with not only chemoselectivity, but also isomeric selectivity. Unlike the Peterson olefination reaction with bis(trimethylsilyl)methyllithium and carbonyl compounds, which produces vinylsilanes with poor E/Z isomeric selectivity,[33] the enhanced stereoselectivity may due to the formation of β-oxidosilane aluminum complexes (Chapter 1, Scheme 1-20) prior to the formation of carbocations (Scheme 2-18). As illustrated in Scheme 2-18, counter-clockwise rotation of the TMS group alleviates steric interactions with the *gem*-dimethyl prior to elimination which accounts for the major Z-isomer formation in the reaction.



Scheme 2-18

Reaction of 9-fluorenone ***2-34*** under the condition given in Table 2-3 afforded vinylsilane ***2-35***, olefin ***2-36***, and β-hydroxysilanes ***2-37*** (Figure 2-5). The β-hydroxysilanes ***2-37*** were isolated by crystallization from the crude product solution after aqueous workup, while ***2-35*** and ***2-36*** apparently polymerized after separation by

chromatography (Prep. TLC or LC with basic alumina). The reaction was repeated three times, and most of the workup procedures were performed under an inert atmosphere of argon; however, we were not able to prevent ***2-35*** and ***2-36*** from polymerizing. It has been noted in the literature that 9-methylenefluorene ***2-34*** and 9-(trimethylsilylmethyl)fluoren-9-ol ***2-37*** are unstable on standing.[58] Before separation by chromatography, ***2-35***, ***2-36***, and ***2-37*** were observed in ^{1}H NMR spectra of the crude product mixture. 9-Fluorenylvinylsilane ***2-35*** was also characterized by GC/ HRMS in the crude mixture. After chromatographic separation, evaporation of the solvent afforded a white film of polymer. The polymer is insoluble in $CDCl_3$ and DMSO- d_6. Analysis by mass spectrometry (EI) indicated the formation of the monomeric units of ***2-35*** and ***2-36*** as well as a dimeric unit of ***2-36***.

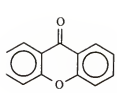


2-34 ***2-35*** ***2-36*** ***2-37***

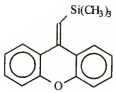
Figure 2-5

Mechanistic Evidence for Carbocation Intermediates

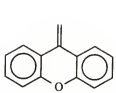
In addition to the reactions mentioned above, 9-xanthone ***2-38*** was examined. Structures of the substrate and likely or observed products are listed in Figure 2-6.



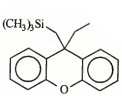
2-38



2-39



2-40



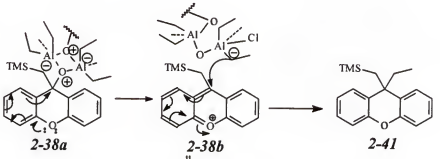
2-41

Figure 2-6

Reaction of xanthone ***2-38*** according to the usual protocol afforded (9-*H*-9-xanthenylidene)trimethylsilane ***2-39***, 9-methylidene-9*H*-xanthene ***2-40***, and 9-trimethylsilylmethyl-9-ethyl-9*H*-xanthene ***2-41***. The vinylsilane product ***2-39*** was only observed in the ^{1}H NMR spectrum of the crude mixture, while the olefin product ***2-40*** was observed in the ^{1}H NMR spectrum and GC/MS of the crude mixture. After purification by prep. TLC, both products may have further transformed to dimers or oligomers (The ^{1}H NMR spectrum was too complicated to analyze). However, the reduction product ***2-41*** was isolated and further characterized by ^{13}C NMR and HR mass spectrometry. The formation of this alkylated product provides additional support for the proposed carbocation ion pair mechanism for the "Abnormal Peterson Olefination" process. The proposed mechanism of the formation of ***2-41*** is summarized in Scheme 2-19.

Mole has previously proposed that the exhaustive methylation of alcohols and ketones with Me_3Al proceeds via carbocation intermediates at elevated temperature (See chapter 1) on the basis of observed skeletal rearrangement. The formation of ***2-41*** strongly suggests that these elimination reactions producing vinylsilanes proceed through an E1-like pathway rather than E2-like or syn-cyclic mechanisms. The carbon bonded to

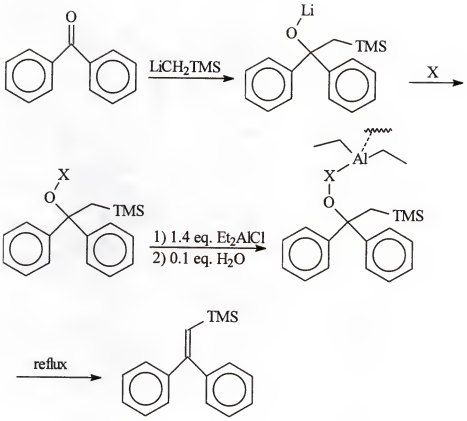
the trimethylsilylmethyl group in ***2-38a*** is a tertiary center. In order to replace the oxygen, the xanthyl cation ***2-38b*** must form prior to ethylation. Although trace amounts of an ethylation product may have been produced in the other diaryl cases, the relatively large amount of ***2-41*** formed in xanthyl case may be accounted for by an expected greater life time for this aromatic cation. In further support of the carbocation mechanism, ketones with electron donating substituents usually give higher yield. This implies intermediates are more likely to be cationic. Although a formal Hammett plot has not been done on our study, the substrate 4,4'-dimethoxybenzophenone gives a higher yield than other ketones.



Scheme 2-19

New Development in the Applications of Organoaluminums in Vinylsilane Synthesis

One of our continuing projects is to lower the reflux temperature for our existing methodology for making vinylsilanes. By adding an extra component, we have tried to make the β-trimethylsilyl alcohol oxygen a better leaving group,[59] so that the reflux temperature can be lowered. The general idea is summarized in Scheme 2-20. So far, we have successfully produced vinylsilanes in good yields at the boiling point of hexanes.

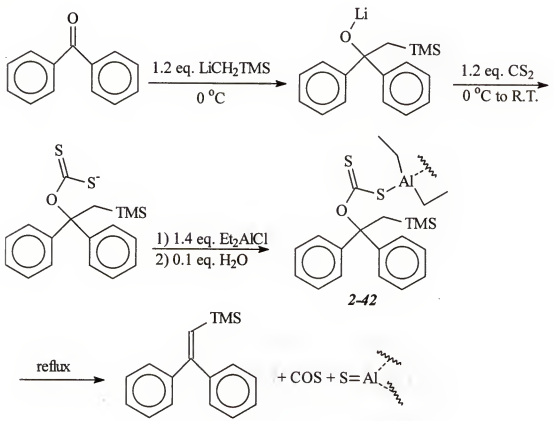


Scheme 2-20

The investigation remains in a prelimmary stage. However, we should be able to better understand and optimize the system in the near future. During the course of study, carbon disulfide, methyl chloroformate, and phenyl chloroformate were allowed to react with β-silylalkoxide anion prior to the addition of Et_2AlCl and H_2O.

Reaction with carbon disulfide (X = CS_2). Benzophenone was employed for testing. Reaction conditions were maintained as previously mentioned with the following exceptions: 1) the addition of 1.2 equivalent of carbon disulfide to the β-silylalkoxide intermediate prior to the addition of alane and water, and 2) hexanes were employed

instead of xylene as solvent. In this study, the reflux reaction of *O*-(1,1-diphenyl-2-trimethylsilyl)ethylxanthate aluminum complex ***2-42*** was expected to decompose to aluminate, carbonyl sulfide, and vinylsilane (Scheme 2-21). After refluxing for 36 hr, 1,1-diphenyl-2-trimethylsilylethanol was recovered as the major product in 76 % yield with 4 % of the expected vinylsilane and 1 % of methylene adduct. Therefore, we decided to employ chloromethyl formate to react with the β-alkoxide anion prior to reflux.



Scheme 2-21

Reactions with methylchloroformate and phenylchloroformate. The reaction conditions in this section remain as previously stated. Methylchloroformate and phenylchloroformate were employed to react with β-silylalkoxide of benzophenone prior

to reflux. A sixteen hour reflux reaction in the presence of phenylchloroformate afforded 38 % vinylsilane and 23 % methylene adduct. In addition, there was an unknown product present in the product mixture which contains TMS and has a ^1H NMR adsorption at 3.8 ppm.

Since the phenylchloroformate reaction result was unsatisfactory, we have concentrated our focus on the methylchloroformate reaction. So far, we are still not able to draw any conclusion. However, the reflux reaction in hexanes was completed in 12 hr with vinylsilane as the major product. In one case, we isolated 67 % vinylsilane and 22 % methylene adduct. Unfortunately, a third unknown product was detected in the majority of the reactions we ran. Since this unknown compound decomposes in the GC column, we have not been able to precisely interpret its GC/MS data. At present, we know that elimination requires the presence of organoaluminums at elevated temperature. Reaction in the absence of organoaluminums afforded β-silylalcohol quantitatively after 24 hr stirring at room temperature. A nineteen hour reflux reaction in the absence of alanes gave a mixture of alcohol, olefin, and vinylsilane in poor chemoselectivity.

Conclusion

Reactions of non enolizable aromatic ketones with trimethylsilylmethyl lithium in xylene gave β trimethylsilyl alkoxide anions. To the alkoxide anions 1.4 eq. of Et_2AlCl was introduced followed by addition of 0.1 eq. H_2O. Reflux reactions of the resulting aluminate solutions afford one carbon-elongated vinylsilanes, instead of the expected Peterson olefination product. This organoaluminum promoted "Abnormal Peterson Olefination" is a stereoselective elimination to give preferred trans products.

The mechanism of this "Abnormal Peterson Olefination" is proposed to proceed via an E1-like pathway producing carbocations as intermediates. It was supported by the ethylation product produced from the reaction of xanthone, and Mole's reports.

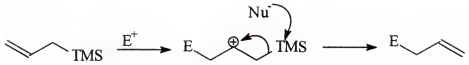
CHAPTER 3
TRANSFORMATION OF KETONES TO ALLYLSILANES

Introduction

In this chapter, the methodology discussed in the last chapter will be applied to the production of allylsilanes. Like vinylsilanes, allylsilanes are important intermediates and reagents in organic synthesis. Similar in reactivity to vinylsilanes, allylsilanes favor substitution over addition, and regiochemistry is usually determined by the site of the silyl group in the starting materials. In allylsilanes, however, hyperconjugative interaction cannot be ignored; the β-silyl effect is a major electronic factor in electrophilic substitution which governs the site of the electrophilic attack. Historically, the first electrophilic substitution (S_E2') of an allylsilane was observed in 1948[60] and the first proof that an allylsilane reacted with allylic shift was reported in 1956.[61]

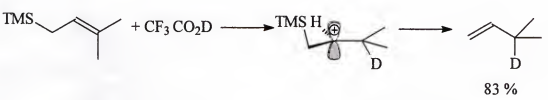
Mechanism

In electrophilic substitution (S_E2') of allylsilanes, electrophiles attack the γ-carbon to create β-silyl carbocations, followed by elimination of the trimethylsilyl group to produce allyl derivatives (Scheme 3-1).[62]



Scheme 3-1

The β-silyl effect provides stabilization of the carbocation intermedaites formed after electrophilic addition. The degree of this hyperconjugative stabilization by silicon is high. The silylethyl cation was calculated to be 38 kcal/mol more stable than the primary ethyl cation,[42] which explains why the silyl groups are readily eliminated instead of hydrogens in electrophilic substitution. The significance of the β-silyl effect is illustrated by the deuterodesilylation of 3,3-dimethylallylsilane as shown in Scheme 3-2. In the reaction, anti-Markovnikov electrophilic attack at the more substituted carbon demonstrates the high degree of stabilization as a result of the β-silyl effect.

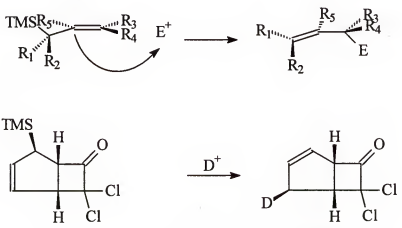


Scheme 3-2

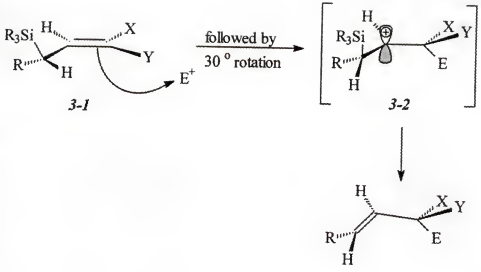
Stereoselectivity

The first investigation of the stereochemistry of electrophilic substitution with allylsilanes (S_E2') was carried out with cyclic allylsilanes, which showed anti and syn stereo-outcomes.[63] In most cases, electrophiles attack acyclic allylsilanes with anti-stereoselectivity (Scheme 3-3). The anti-stereoselectivity was examined with deuterons,

protons, and several other electrophiles.[64] A simple justification for the anti stereo-outcome involves reaction of the most stable conformation of the allylsilane with electrophiles (Scheme 3-4). The preferred conformation ***3-1***, shown in Scheme 3-4, has hydrogen eclipsing the double bond. The large silyl group influences electrophilic attack on the lower surface; then the silyl group rotates 30° to transform to ***3-2*** followed by desilylation to give the product. The overall reaction is anti stereoselective. However, R has to be much larger than a hydrogen atom and Y can not be hydrogen. These conditions are required to achieve the observed anti selectivity.



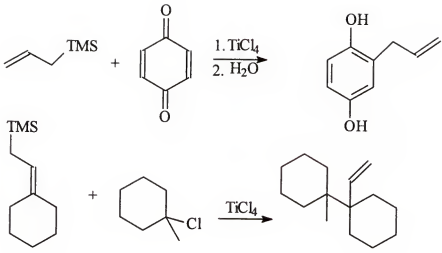
Scheme 3-3



Scheme 3-4

Application of Allylsilanes in Organic Synthesis

Allylsilanes are fairly stable and relatively inert to air and moisture. They are versatile synthetic intermediates since they react with a variety of electrophiles such as carbocations, acetals and ketals, and ketones and aldehydes. Additionally, they can be employed for intramolecular cyclization. Examples of allylsilanes in organic transformations are shown in Scheme 3-5.[62]

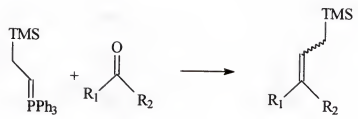


Scheme 3-5

Preparations of Allylsilanes

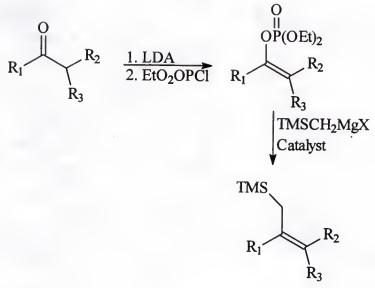
The use of the allylsilanes in organic synthesis started in 1970 as a result of the pioneering efforts of Calas,[65] Corrriu,[66] Sakurai,[67] and Fleming.[25] Since then numerous investigations have been performed on the preparation and general use of allylsilanes as synthetic intermediates and reagents in organic synthesis. Allylsilanes can be prepared by employing one of a number of techniques that include, the Wittig reaction, transition metal catalyzed cross-coupling reactions, hydrosilylation reactions, reductive elimination of β-hydroxysulfones, and β-hydroxyselenides, and organometallic reagents.[68]

Wittig reaction. Wittig reactions of (2-trimethylsilylethylidene)triphenylphosphorane and carbonyl compounds have been employed extensively in the preparation of terminally substituted allylsilanes.[69] This Wittig reagent reacts well with aldehydes and reactive ketones (Scheme 3-6).



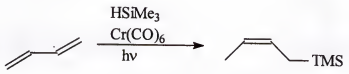
Scheme 3-6

Transition metal catalyzed cross-coupling reactions. Reactions of enolizable ketones with LDA followed by addition of chlorophosphates afford enol phosphates. Enol phosphates can then be transformed to allylsilanes by reacting them with trimethylsilylmethylmagnesium halides in the presence of transition metal catalysts (Scheme 3-7).[70] Such catalysts include nickel(II) and palladium(0). This method is appropriate for compounds with reactive functional groups such as α,β-unsaturated ketones and esters, allylalcohols, or arylbromides.



Scheme 3-7

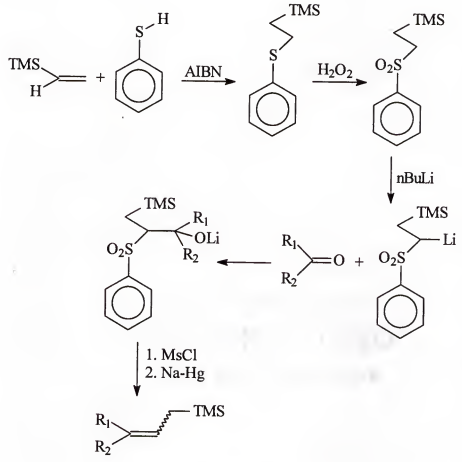
Hydrosilylation reaction. Hydrosilylation of 1,3-dienes proceeds in a 1,4-fashion in the presence of transition metal catalysts to produce allylsilanes.[71] An example is shown in Scheme 3-8



Scheme 3-8

Reductive Elimination of β-hydroxy Sulfones and Selenides

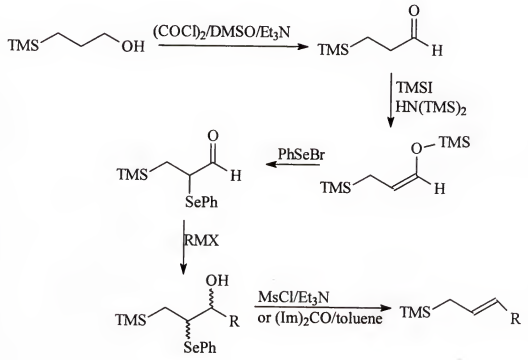
Hsiano and Shechter[72] reported a synthetic method involving conversion of aldehydes and ketones to the corresponding β-hydroxy sulfones. Reaction of the β-hydroxy sulfones with MsCl followed by reductive elimination with sodium amalgam (6%) afforded the corresponding allylsilanes (Scheme 3-9).



Scheme 3-9

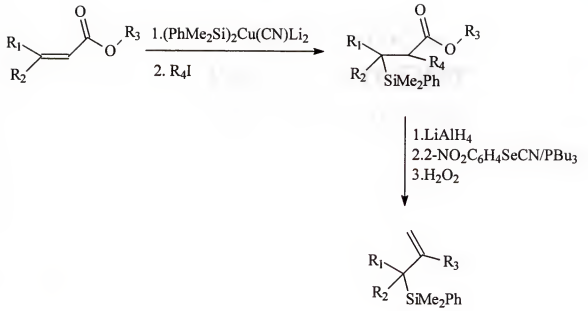
In 1987, Sarkar and Ghosh[73] developed a synthetic method involving reaction of β-hydroxyselenides with MsCl/Et_3N to produce the corresponding allylsilanes. This method not only introduces the allylsilane function α to the carbonyl group, but also

produces E-allylsilanes (Scheme 3-10). Rather than treating the β-hydroxyselenides with $MsCl/Et_3N$, it was reported[74] that β-hydroxyselenides can be converted to allylsilanes by reacting them with *N,N'*-carbonylidiimidazole.



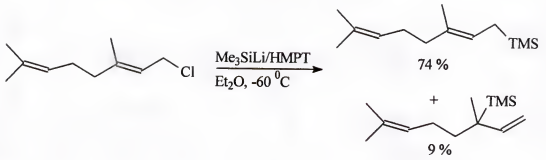
Scheme 3-10

Via silylcuprate reagents. Allylsilanes can be prepared by organometallic reagents such as silylcuprates.[75] The silylcuprate reagent undergoes 1,4-addition with α,β-unsaturated esters to produce enolates. The enolates are then alkylated or protonated to afford the corresponding esters. Reduction of the esters by lithium aluminum hydrides followed by Grieco dehydration (reaction with 2-nitrophenylselenocyanate and hydrogen peroxide) produces the corresponding allylsilanes (Scheme 3-11).



Scheme 3-11

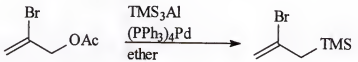
Via organolithium reagents. Trimethylsilyllithium can be prepared from the reaction of hexamethyldisilane and methyllithium in HMPT with ether as co-solvent. Metathesis reactions of trimethylsilyllithium with allylhalides afford allylsilanes.[76] Although this is a direct method for the production of allylsilanes, allylhalides such as secondary halides give a complicated mixture of products (Scheme 3-12). Therefore, care must be taken to obtain the desired product.



Scheme 3-12

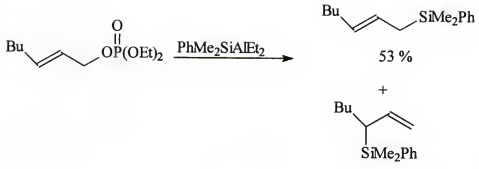
Via organoaluminum reagents.

Direct transformations of allylic acetates. Allylsilanes can be produced by reactions of allylic acetates with tris(trimethylsilyl)aluminum in the presence of transition metal catalysts (Scheme 3-13).[77] This is a highly chemoselective transformation which will not affect acetals, enones, esters, and isolated double bonds in the substrates (Scheme 3-13).



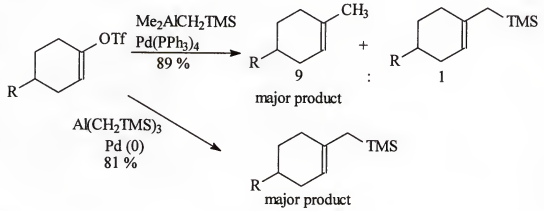
Scheme 3-13

Coupling reactions of allylic phosphates. Another application of organoaluminums in allylsilane synthesis involves coupling reactions of allylic phosphates with silicon-aluminum reagent.[78] The yields are usually good but exhibit poor regioselectivity (Scheme 3-15).



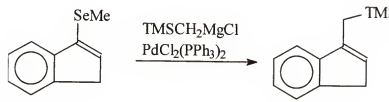
Scheme 3-15

Cross coupling reactions of vinyl triflates. Saulnier and coworkers[79] developed a cross-coupling reaction of vinyl triflates with tris(trimethylsilylmethyl)aluminum in the presence of Pd(0) catalyst to produce the corresponding allylsilanes in good yields. The aluminum complex is prepared in situ from 3 eq. of Me_3SiCH_2Li and 1 eq. of $AlCl_3$, reacts with vinyl triflates to give the corresponding allylsilane (Scheme 3-16).



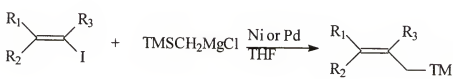
Scheme 3-16

Nickel and palladium catalyzed coupling reaction of vinyl selenides. Hevesi and coworkers[80] reported a method involving the coupling of vinyl selenides with trimethylsilylmethylmagnesium chloride in the presence of Ni(II) or Pd(II) catalysts to produce allylsilanes (Scheme 3-17).



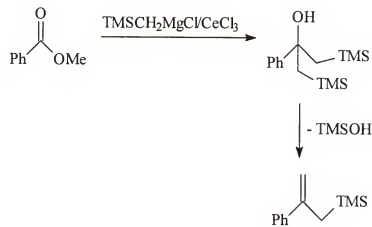
Scheme 3-17

Reaction of alkenyl iodides with trimethylsilylmethylmagnesium chloride in the presence of catalysts. Negishi and coworkers[70] developed a method involving reactions of alkenyl iodides with trimethylsilylmethylmagnesium chloride in the presence Ni or Pd catalysts producing allylsilanes in good yields. This method is stereo- and regioselective (Scheme 3-18a).



Scheme 3-18a

Cerium catalyzed conversion of esters. Bunnelle and Narayanan[81] developed a method employing a complex of $CeCl_3$ and $TMSCH_2MgCl$ to convert esters to the corresponding allylsilanes (Scheme 3-19). However, they note that this method was limited to the use of the complex of $CeCl_3$ and $TMSCH_2MgCl$. The complex of $CeCl_3$ and $TMSCH_2Li$ was reported to give poor results.



Scheme 3-19

Organoaluminums Promoted "Abnormal Peterson Olefination" in Allylsilanes Synthesis

During our investigation of the synthesis of vinylsilanes, applying the same methodology in vinylsilane synthesis, we discovered reactions of aromatic ketones with enolizable protons which produce the corresponding allylsilanes.

Preliminary Investigation

Intense investigations of acetophenone ***3-3*** reactions comprised most of our early studies (Figure 3-1). The results of the numerous reactions performed are given in Table 3-1. The general reaction procedures were similar to those discussed in Chapter 2, i.e. ***3-3*** was treated with 1.2 eq. of $LiCH_2TMS$ followed by 1.4 eq. of Et_2AlCl in the presence of ether with reflux overnight. The products were identified based on GC/MS and ^1H NMR results compared to reported literature values.

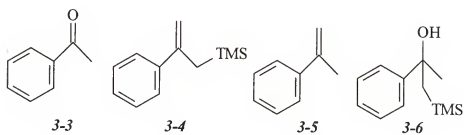


Figure 3-1

Table 3-1. Preliminary studies on reactions of acetophenone ***3-3***.[a]

Entry	Solvents	Reflux hours	%[b]  ***3-4***	%[b]  ***3-5***	%[b]  ***3-6***
1[c]	30 mL hexanes	16	34	Small trace	-
2[c]	30 mL toluene	16	11	-	-
3[c]	30 mL hexanes	84	10	25	-
4	20 mL hexanes, 20 mL ether	12	2	Small trace	24
5	40 mL hexanes, 5 mL ether	48	1	11	-
6[d]	30 mL hexanes	7.5	24	41	-
7[e]	40 mL hexanes, 5 mL ether	30	3	1	-
8[e]	40 mL benzene, 5 mL ether	14	24	2	-

[a] 0.5 g, 4.2 mmol of ketone.
[b] yield was determined by ^{1}H NMR with known amount of anisole as internal standard.
[c] an aged bottle of Et_2AlCl was employed.
[d] 2 eq. Et_2AlCl was used instead of 1.4 eq.
[e] 1.4 eq. Me_3Al was added in addition to 1.4 eq. Et_2AlCl.

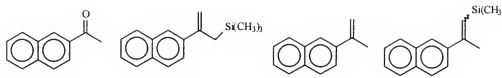
Reaction of 1-indanone was also included in our initial studies. The reaction was refluxed using a mixture of 30 mL of benzene and 5 mL of ether for 3 days to afford 63 % of the corresponding allylsilane.

Reactions of acetophenone employing an aged Et_2AlCl reagent (alumoxanes should be present in the bottle) afforded mainly the 2-phenylallylsilane ***3-4***. Moreover, addition of ether to the solution mixtures afforded mainly allylsilanes as major products, but the yields were unsatisfactory. Based on our experimental results, we believed that if we promoted the aggregation of the aluminum complexes without lowering the reflux temperature, both the regioselectivity and yield of the reactions should improve.

Therefore, we decided to introduce trace amounts of water into the system prior to reflux as previously discussed (Chapter 2).

Organoaluminum Promoted "Abnormal Peterson Olefination": Allylsilanes

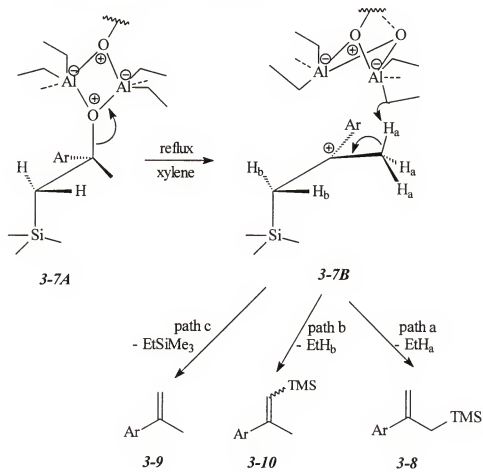
During our preliminary investigations, we did not employ cerium trichloride to fulfill the addition step; nevertheless, cerium chloride is used extensively in our current study. Controlled hydrolysis of the aluminum complexes prior to reflux was first attempted with the reactions of benzophenone (Chapter 2). After obtaining satisfactory results, acetophenone ***3-3*** was tested again with the same general method with the exception that the xylene/acetophenone solution was cooled to –78 °C prior the introduction of 1.2 eq. of $LiCH_2TMS$. After workup, the solvent was evaporated, and the yield of the 1-phenylallylsilanes ***3-4*** was determined to be 17 % by ^1H NMR using anisole as the internal standard. This unsatisfactory result was determined to be caused by the evaporation of the products, since the final weight of the product mixture was considerably less than the weight of the starting materials. Therefore, we chose 2-acetonaphthone ***3-7*** to carry on the investigation. Since this starting material has a boiling point of 300-301°C, the corresponding allylsilane ***3-8*** is less likely to evaporate during solvent removal. The reaction of ***3-7*** according to the usual protocol afforded allylsilane ***3-8*** (65 %), olefin ***3-9*** (8 %), and the vinylsilanes ***3-10*** (3 %) shown in Figure 4-2. These products were detected by ^1H NMR and GC/MS, the latter of which indicated four products in the mixture, namely ***3-8***, ***3-9***, and E/Z isomers of ***3-10***. No recovered alcohol was detected. However, the allylsilane was our primary interest and we continued our investigations on other ketones.



3-7 *3-8* *3-9* *3-10*

Figure 3-2

To account for the formation of the allylsilane and other possible products, we propose the following mechanisms (Scheme 3-20).



3-7A *3-7B*

3-9 *3-10* *3-8*

Scheme 3-20

Due to the stereoelectronic influence, complex ***3-7A*** should be the most stable conformer in which the bulky trimethylsilyl group is *anti* to the oligomeric oxy-aluminum complexes. At elevated temperature, ***3-7A*** disintegrates into anionic alumoxane and carbocation ***3-7B***. This intimate ion pair then undergoes abstraction of a proton (H_a, path a; H_b, path b) or silyl group (path c) to form alkene adducts. In path a shown in Scheme 3-20, the hydrogen on the methyl group aligned with the empty p-orbital is abstracted through an intramolecular E-1 like elimination to form the corresponding allylsilane ***3-8***. Path b requires a 30° rotation of the carbon bonded to silicon. This rotation weakens the β-silyl effect prior to intramolecular proton abstraction to give the corresponding vinylsilane ***3-10***. Due to the stereoelectronic factor, the silicon group is more likely to be abstracted by organoaluminums, as illustrated in path c, in an intermolecular manner to afford olefin ***3-9***. Among these possibilities, path a dominates because of the stereoelectronic and entropy factors (intramolecular vs. intermolecular); therefore, this reaction is highly regioselective and chemoselective, producing allylsilane in good yield in an acylic system.

In addition to acetophenone and 2-acetonaphthone, 1-indanone ***3-11***, 1-(4-chlorophenyl)ethanone ***3-15***, and 1-adamantyl methyl ketone ***3-19*** were tested during our preliminary study. The structures of the compounds and results are listed in Figure 3-3 and Table 3-2

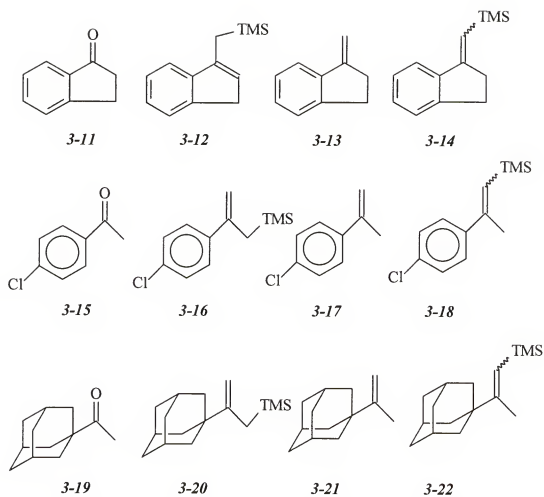

O
TMS
TMS
3-11
3-12
3-13
3-14
O
Cl
TMS
Cl
Cl
TMS
3-15
3-16
3-17
3-18
O
TMS
TMS
3-19
3-20
3-21
3-22

Figure 3-3

Table 3-2. Preliminary study of Organoaluminum Promoted "Abnormal Peterson Olefination" in the Synthesis of Allylsilanes.

Substrate[a]	Reflux time	% of allylsilane[b]	% of olefin[b]	% of vinylsilanes (E/Z)[b]
 ***3-11***	24	53	Small trace	Small trace
 ***3-15***	24	55	Small trace	2
 ***3-19***	74	53	2	40

[a] all substrates are of 0.1 M in xylene.
[b] yields are determined by ^{1}H NMR with known amounts of anisole as internal standard.

Reaction of 1-adamantyl methyl ketone *3-19*

Two sets of major vinyl proton signals (allyl- and vinyl- silane alkene protons) were observed in the ^{1}H NMR spectrum which correspond to 53 % and 40 % of the product isomers. GC/MS data clearly indicated the presence of a small amount of 1-isopropenyladamantane ***3-21*** and two other major products (same mass) with similar retention times. An Attached Proton Test was performed to examine the mixture. A tertiary carbon signal (down) (CHTMS) appearing at 118.7 ppm indicated that 1-

adamantyl-1-methylvinylsilanes ***3-22*** should be the minor product of the reaction. Experimental procedures will be discussed in greater detail later in the chapter.

Application of Cerium trichloride in Organoaluminums Promoted "Abnormal Peterson Olefination" in the Synthesis of Allylsilanes

Results from the preliminary study suggested that alkylation of the enolizable ketone was problematic. In the case of substrate ***3-11 and 3-15***, the reactions afford product in respectable yields; however, we believed that these yields could be optimized if the degree of enolization of the ketone was decreased. Organocerium reagents are widely employed to facilitate alkylation of enolizable ketones in high yields. Incorporation of this methodology with our procedures provides the basis for our current investigation.

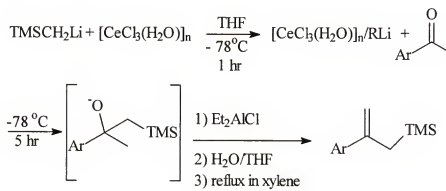
Organocerium Chloride

Cerium, a lanthanide series element, is a shiny gray, malleable, ductile and soft metal which is ranked first on the abundance chart for rare earth metal found in the earth's crust. The oxide form was discovered in 1803 by Jön Jacob Berzelius. Physical properties of anhydrous cerium chloride were reported in 1928.[82] Organocerium reagents are prepared *in situ* by the reaction of organolithium with anhydrous cerium chloride or cerium iodide. Cerium chloride is preferred, as preparation of the iodide requires the handling of pyrophoric cerium metal.[83] At present the identity and purity of the reagent written as $RLi/CeCl_3$ is not well established. Heating cerium chloride heptahydrate $CeCl_3 \bullet 7H_2O$ at 150 °C for 12 hr and 0.03 torr (a literature procedure) produces a colorless powder which has the formula $[CeCl_3(H_2O)]_n$.[84] So far, correct structures of

these powder have not been determined. However, this reagent should be referred to as $[CeCl_3(H_2O)]_n$/RLi.

[(Trimethylsilyl)methyl]lithium/Cerium Chloride incorporated Organoaluminums Promoted "Abnormal Peterson Olefination" in Allylsilane Synthesis.

We have slightly modified the preparation of [(trimethylsilyl)methyl]lithium/cerium chloride reported by Johnson[85] for alkylation of enolizable ketones. The experimental procedures, summarized in Scheme 3-21, will be discussed in detail in Chapter 4.



Scheme 3-21

We have employed this method to reinvestigate the compounds mentioned in the beginning of this chapter. In general, yields with this method are higher than those without organocerium reagent facilitating the alkylation step. Several other enolizable ketones were tested, the results and products of which are were listed in Table 3-3 and Figure 3-4.

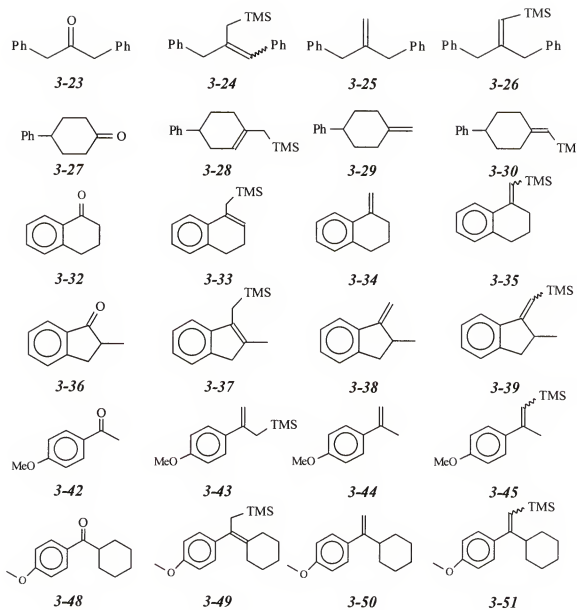
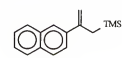
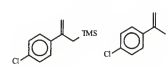

3-23
3-24
3-25
3-26
3-27
3-28
3-29
3-30
3-32
3-33
3-34
3-35
3-36
3-37
3-38
3-39
3-42
3-43
3-44
3-45
3-48
3-49
3-50
3-51

Figure 3-4

Table 3-3. Organocerium incorporated Organoaluminum Promoted "Abnormal Peterson Olefination" in the Synthesis of Allylsilanes.

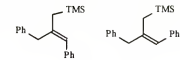
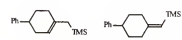
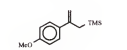
Substrates[a]	Reflux time (hr)	Yield (isolated yields, unless otherwise noted)	Product distribution[c]
	36	78 %[b]	
3-7			***3-8***
	24	75 %[b]	
3-11			***3-12***
	36	70 %	
3-15			***3-16*** : ***3-17*** 6 : 1
	96	48 %	
3-19			***3-20*** : ***3-22*** 7 : 1

[a] 0.1 M of substrate in xylene

[b] yield determined by ^{1}H NMR with known amount of anisole as internal standard.

[c] each reaction afforded </= 3 % of olefins and vinylsilanes unless otherwise noted, product ratios are determined by ^{1}H NMR.

Table 3-3. Organocerium incorporated Organoaluminum Promoted "Abnormal Peterson Olefination" in the Synthesis of Allylsilanes.

Substrates[a]	Reflux time (hr)	Yield (isolated yields, unless otherwise noted)	Product distribution[b]
	36	74 %	
3-23			***3-24E*** : ***3-24Z***
			1 : 3
	48	79 %	
3-27			***3-28*** : ***3-30***
			1 : 1.3
	41	61 %	
3-32			***3-33*** : ***3-35***
			3.4 : 1
	36	55 %	
3-36			***3-37***
	36	59 %	
3-42			***3-43***

[a] 0.1 M of substrate in xylene

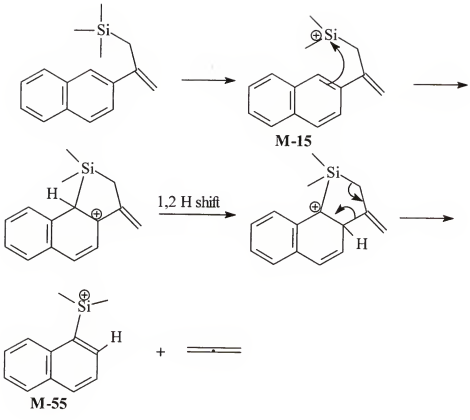
[b] each reaction afforded </= 3 % of olefins and vinylsilanes unless otherwise noted, product ratio is determined by ^{1}H NMR.

1-Adamantyl methyl ketone *3-19*

One portion of our study involved a second investigation of the reaction of 1-adamantyl methyl ketone ***3-19***. In this subsequent experiment, a ninety six hour reflux reaction afforded 48 % yield of a mixture of [2-(1-adamantyl)allyl]trimethylsilane ***3-20*** and [2-(1-adamantyl)methyl]vinyltrimethylsilane ***3-22*** in 7:1 ratio. By contrast, the method developed by Bunnelle,[81] (mentioned in this chapter) employs a cerium catalyzed conversion of esters to allylsilane was incapable of producing ***3-20***. Despite a longer reaction time than other methods, ours is a viable and economical method. GC/MS data indicated the aforementioned two isomers as major components. To identify these isomers, ^{1}H NMR, ^{13}C NMR and Attached Proton Test (APT) were conducted. In ^{1}H NMR, adsorptions at δ (0.058, 9H, CH_3Si), (0.120, 9H, CH_3Si), (4.587, 1H), (4.709, 1H), (5.202, 1H) clearly indicated the presence of two TMS containing isomers with ***3-20*** as the major product. APT and "Quantitative" ^{13}C NMR further support this assignment. In the APT experiment [CH_3, CH (down); CH_2, C (up)], only one of the four peaks [105.51 (up, ***3-20***), 118.75 (down, ***3-22***), 115.95 (up, ***3-20***), 163.43 (up, ***3-22***)] in the alkene adsorption region representing the four sp^2 carbons in vinylsilane ***3-22*** (**C**=**C**HTMS) and in allylsilane ***3-20*** (**C**=**C**H_2). A "Quantitative" ^{13}C experiment was used to establish the relationship between integrated peak areas and the number of nuclei under those areas. To perform this experiment, the instrument was set to allow ten seconds between pulses for relaxation, with decoupling only during the acquisition. The resulting spectrum showed the overall peak areas of ***3-20*** were much greater than ***3-22***; therefore, establishing that ***3-20*** was the major isomer in the reaction products.

2-Acetonaphthone *3-7*, 1-indanone *3-11*, and p-chloroacetophenone *3-15*

During our reinvestigation on substrates 2-acetonaphthone ***3-7***, 1-indanone ***3-11***,[87] and p-chloroacetophenone ***3-15***, we observed a consistent 10 % increase in reaction yields. Another observation is a correlation between reflux reaction time and reaction yields relative to the amount of moisture in pre-dehydrated cerium chloride. We dehydrated cerium chloride according to literature procedures and stored this product in a desiccator in our dry box. Since our dry box is not completely air free, stored cerium chloride absorbed moisture over a period of time. Although merely speculations, reactions using freshly dehydrated cerium chloride seemed to require less reflux reaction times and gave higher yields. In the reaction of 1-indanone ***3-11***, we noticed that the reaction using freshly dehydrated cerium chloride was consistently complete in 24 hr and afforded 75 % yield, while the reaction with aged reagent required a 36 hr reflux and afforded only 40 % yield. If this speculation is correct, addition of 0.1 equivalent of H_2O may not be necessary. This hypothesis will be tested in the future. It is worth noticing that the mass spectra for allylsilanes derived from 2-acetonaphthone ***3-7***, p-methoxyphenyl methyl ketone ***3-42***, and p-chloroacetophenone ***3-15*** gave M-55 peaks. This may be due to the loss of a methyl group to form a cation to give a M-15 peak. Then a cation rearrangement followed by fragmentation again to lose allene would give the M-55 peaks as shown below.



1,3-Diphenyl-2-propanone *3-23*

A thirty-six hour reaction of 1,3-diphenyl-2-propanone ***3-23*** at reflux afforded 74 % of a mixture of *E/Z* 2-benzyl-3-phenyl-2-propenyl-1-trimethylsilane ***3-24*** in 1:3 ratio, respectively. GC/MS data revealed the presence of two allylsilane isomers as major components, and vinylsilane and starting silylated alcohol as minor components. Nuclear Overhauser Effect experiments were performed to determine *E* and *Z* configuration (Figure 3-5).

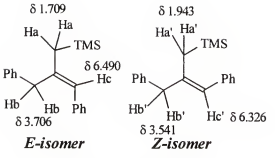


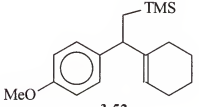
Figure 3-5

Irradiation at δ 6.326 and δ 6.490 enhanced the signal at δ 3.541 and δ 1.709, respectively, by 3 %. These results indicated the *Z*-isomer was the major isomer. In addition, since protodesilylation transforms isomeric allyl- and vinyl-silanes to the same alkene. The above product mixture was generally reacted with trifluoroacetic acid (TFA) at the same scale present in the NMR tube to effect desilylation. Reaction of the product mixture with 2 drops of TFA in an NMR tube caused three vinyl proton signals, δ 5.581 vinylsilane vinyl-proton (10 % yield), δ 6.326 *Z*-allylsilane vinyl-proton (56 % yield), and δ 6.490 *E*-allylsilane (19 % yield) vinyl-proton, to diminish as a new vinyl-proton signal grew at δ 4.898. The new signals at δ 4.898 and 3.329 indicated the formation of 2-benzyl-3-phenyl-2-propene generated,[86] the expected desiylation product of E/Z ***3-24*** and the vinylsilane minor isomer.

p-Methoxyphenyl cyclohexyl ketone *3-48*

Reaction of p-anisaldehyde with cyclohexyl magnesium bromide afforded p-methoxy cyclohexyl methanol ***3-46*** in 87 % yield. PCC oxidation of ***3-46*** gave p-methoxyphenyl cyclohexyl ketone ***3-48*** in 74 % yield. The usual conditions with a fourty-six hour reflux reaction of ***3-48*** afforded a mixture of several compounds with

vinylsilane as the major product. Results obtained from these experiment were reproducible. GC/MS data suggested the presence of five compounds; four of which contained the trimethylsilyl group. Tentatively, these have been indentified as 1-(p-methoxyphenyl)-1-cyclohexylethene ***3-50***, 2-(p-methoxyphenyl)-2-cyclohexyl vinyltrimethylsilane ***3-51*** ***E/Z***, 2-trimethylsilylmethyl-2-p-methoxyphenylmethylenecyclohexane ***3-49***, and 2-cyclohexenyl-2-p-methoxyphenyl-1-trimethylsilylethane ***3-52***. The results were supported by ^{1}H NMR data. Since our primary interest is exploration of the methodology of organoaluminum promoted allylsilane synthesis, we did not further investigate this reaction. However, an explanation of these results is provided later in this chapter.

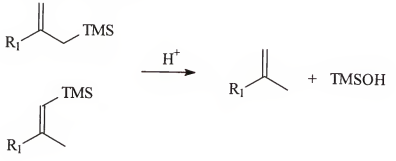


3-52

Tetralone *3-32*

A forty one hour reflux reaction of tetralone ***3-32*** yielded a mixture of compounds with (3,4-dihydronaphthal-1-ylmethyl)trimethylsilane[87] ***3-33*** as the major isomer. ^{1}H NMR and GC/MS data suggested the presence of *E/Z* (1-trimethylsilylmethylene)-1,2,3,4-tetrahydronapthalene ***3-35*** as a minor component and a small trace of 1-naphthylmethyltrimethylsilane.[88] Reaction of the product mixture with TFA (Protodesilylation) caused three vinyl proton peaks at δ 5.887 (vinylsilane vinyl proton), δ 6.090 (allylsilane vinyl proton) (triplet), and δ 6.500 (vinylsilane vinyl proton) to diminish as two new vinyl proton signals grew. This represented transformations of allyl-

and vinyl-silanes to 1-methylene-1,2,3,4-tetrahydronapthalene[89] ***3-34***, and further supported the identities of these isomers. A proposed mechanism is suggested in the next section to explain the observed result.

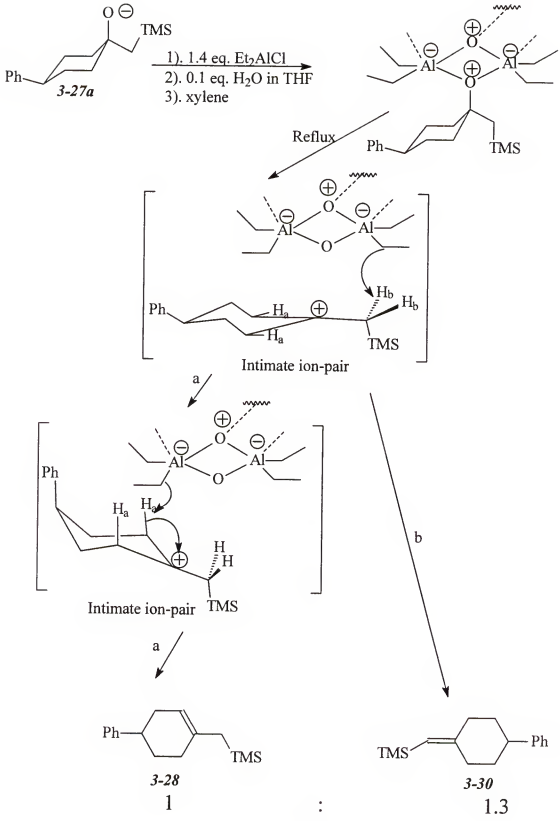


Protodesilylation

4-Phenylcyclohexanone *3-27*

Reaction of 4-phenylcyclohexanone ***3-27*** after 36 hr reflux yielded a 3.4 : 1 mixture of 4-phenyl-1-(trimethylsilylmethyl)-1-cyclohexene[79] ***3-28*** and 4-phenyl-1-(trimethylsilylmethylene)cyclohexane ***3-30*** in 79 % yield. This assignment was secured by GC/MS, HRMS, ^{1}H NMR and ^{13}C NMR data relative to reported literature values. Moreover, 1-(trimethylsilylmethyl)-4-phenylcyclohexanol ***3-31*** was made by the reaction of 4-phenylcyclohexanone ***3-27*** with trimethylsilylmethyl lithium/ cerium chloride in 98 % yield. The alcohol was then reacted with $HF_{(aq)}$ in acetonitrile to produce 1-methylene-4-phenylcyclohexane ***3-29***[90] in 59 % yield. The spectral data of the TMS alcohol ***3-31*** and 1-methylene-4-phenylcyclohexane ***3-29*** further support the reliability of the assignments of ***3-28*** and ***3-30***. To explain the observed poor regioselectivity in this reaction as well as reactions of p-methoxyphenyl cyclohexyl ketone ***3-46*** and tetralone ***3-32***, a syn E1-like mechanism is proposed and is shown in Scheme 3-22. As illustrated in Scheme 3-22, an intimate ion pair forms upon reflux. Two sets of protons (H_a and H_b) are

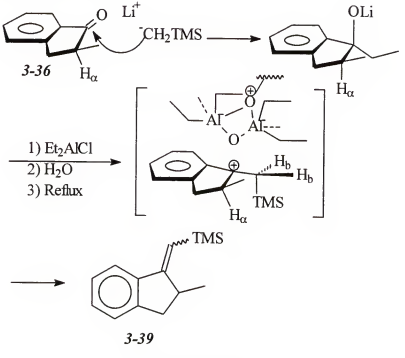
available for abstraction to form a double bond. Path b involves a 30° rotation of the silylated carbon followed by a proton (H_b) abstraction to form a vinylsilane ***3-30***. Path a involves a chair-chair conformation followed by an axial proton (H_a) abstraction to yield an allylsilane ***3-28***. Since there are two available elimination pathways, a mixture of allyl- and vinyl- silanes is inevitably produced.


TMS
Ph
3-27a
1). 1.4 eq. Et2AlCl
2). 0.1 eq. H2O in THF
3). xylene
Reflux
Ph
TMS
Hb
Ha
Intimate ion-pair
a
b
Intimate ion-pair
a
3-28
3-30
1 : 1.3

Scheme 3-22

2-Methyl-1-indanone *3-36*

To further support the proposed syn-E1-like mechanism, 2-methyl-1-indanone ***3-36*** was examined with the expectation that the vinylsilane would be major component and allylsilane the minor component. The anticipated product distribution results from the *anti*-relation of the α-proton (H_α) to the oxygen anion in the intermediate, which is generated by the steric bias in the addition of the trimethylsilylmethyl anion (Scheme 3-23). Since abstraction of H_b is a facile intramolecular process, vinylsilane ***3-39*** would be the more likely major product.



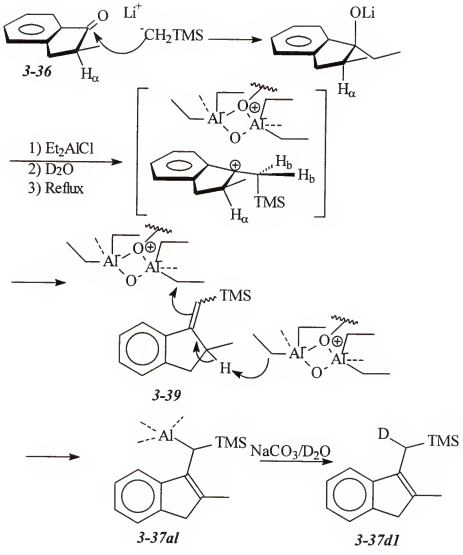
Scheme 3-23

Surprisingly, the allylsilane was obtained as the major product in the first run, however, an approximately 1:1 mixture of allylsilane (in slight excess) and vinylsilanes (*E* and *Z*) was obtained when the reaction was subsequently repeated under the same conditions

(three separate reactions). An NMR scale reaction was performed by allowing 2 drops of 1:1 product mixture to react with 3 drops of TFA for three hours, which resulted in the disappearance of the allylsilane and the vinylsilane vinyl proton signals. A new set of signals: [^{1}H NMR δ 2.02 (s, 3 H), 2.05 (s, 3H), 3.24 (s, 2H), 7.36 (m, 4H) and ^{13}C δ 147.539, 142.318, 137.978, 132.439, 126.034, 123.545, 122.953, 117.900, 42.413, 13.822, 10.073] appeared consistent with the formation of 2,3-dimethyl-1*H*-indene,[91] thus supporting the assignment of the allyl- and vinyl-silanes. It is worth noting that isomerization of vinylsilane to allylsilane may occur in a slightly acidic medium, such as in aged $CDCl_3$ solvent. This could well explain allylsilane as the major product of the first reaction. The isomerization of vinylsilanes was observed when a product mixture reacted with equal molar of TFA in ether for two hours or allowed to solvate in $CDCl_3$ for several hours. One reaction yielded an approximately 1:1 mixture of vinylsilane and allylsilane. This mixture was purified by ethyl acetate deactivated silica gel column. After purification by chromatography was completed, ^{1}H NMR data indicated the ratio of vinylsilane to allylsilane reduced to 1 : 2 with the presence of small amounts of methylene adduct.

As previously mentioned, the vinylsilane was expected to be the major product from the reaction of 2-methyl-1-indanone with $TMSCH_2Li$/ $CeCl_3$ due to the syn E1-like elimination process promoted by the alane Et_2AlCl. Results of approximately 1 : 1 mixture of allylsilane (slightly favored product) and vinylsilane suggested the existence of an alternative pathway to that suggested in Scheme 3-23. To explore the basis for the unexpected product distribution result, we conducted several experiments. First we examined the possibility of isomerization of vinylsilane ***3-39*** to allylsilane ***3-37*** under

the reasonable basic conditions of the reaction medium (Scheme 3-24). Reaction procedures were generally kept the same; except 0.1 equivalent of D_2O in THF was used instead of H_2O. Also, 0.5 % $NaHCO_3$ in D_2O was used for the workup. As illustrated in Scheme 3-24, if an allylic proton is abstracted by an aluminum species to afford ***3-37al*** a deuteriated allylsilane should be afforded upon quenching with $NaHCO_3/D_2O$. As mentioned in chapter one, the basicity of alkyl groups on organoaluminums decreases with increasing number of heteroatoms bonded to aluminum atoms and with decreasing number of alkyl groups in aluminum complexes. Moreover, the pKa at the allylic position of the vinylsilane is approximately 40.[92] Therefore, we anticipated that isomerization of vinylsilane to allylsilane should not be the major pathway producing the isolated product and that only small amounts of deuteriated product would be detected in the allylsilane product ***3-37***.

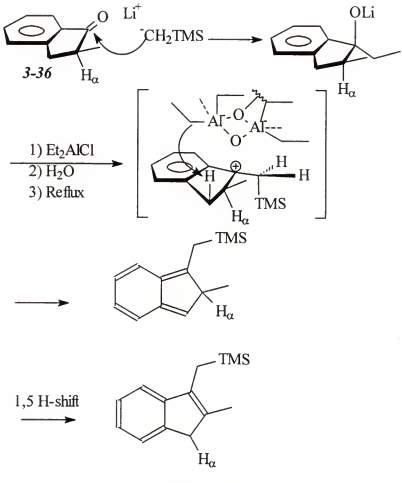


Scheme 3-24

If isomerization is the major pathway to produce allylsilane, the peak area at δ 2.014 ppm, which corresponds to the hydrogen absorption at the α-carbon to the TMS group, will reduce by half compared to the non-deuteriated allylsilane . ^{1}H NMR data revealed the product mixture contained approximately equal amounts of allylsilane and vinylsilanes. By comparing the peak area at δ 2.014 ppm relative to other proton peak

areas, no apparent changes were found. This demonstrated isomerization shown in Scheme 3-24 was not the major pathway for the formation of allylsilane.

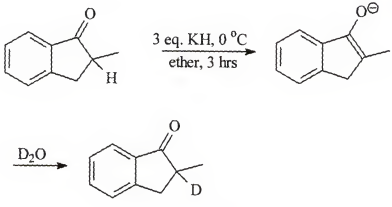
A remaining mechanistic explanation for the formation of allylsilane is the benzylic proton abstraction followed by 1,5-sigmatropic shift of hydrogen[93] to give allylsilane (Scheme 3-25).



Scheme 3-25

To examine this possibility, 2-deuterio-2-methyl-1-indanone was prepared, as shown in Scheme 3-26, by deprotonation of 2-methyl-1-indanone with potassium hydride at 0 °C generating the corresponding enolate, which was then quenched with deuterium

oxide. The reaction afforded 93 % recovery of ketone with 77 % deuteriation (% of deuterium was determined by GC/MS[94]). The ^{1}H NMR spectrum of 2-methyl-1-indanone (C_6D_6) consists of a methyl signal at δ 1.064 ppm (d), a benzylic hydrogen signal at δ 2.121 ppm (dd), an enolizable hydrogen signal at δ 2.25 ppm (m), and a second benzylic hydrogen signal at δ 2.714 ppm (dd) in addition to aromatic proton signals. After deuteriation, the AMX system (^{1}H NMR pattern) of 2-methyl-1-indanone was replaced by an AX system (C_6D_6) which consists of a methyl signal at δ 1.050 ppm (s), a benzylic hydrogen signal at δ 2.118 ppm (d), a second benzylic hydrogen signal at δ 2.714 ppm (d), in addition to the aromatic proton signals. Moreover, successful transformation to 1-deuterio-2-methyl-1-indanone was also supported by ^{13}C NMR data, in which the strong α carbon signal (C(O)**C**HCH$_3$) at δ 41.864 ppm of 2-methyl-1-indanone was replaced by the weak triplet signal of product (C(O)**C**DCH$_3$).

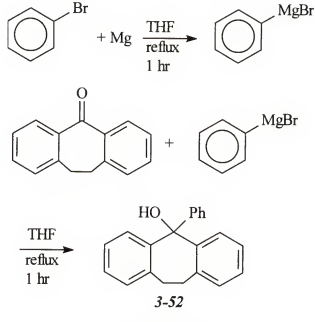


Scheme 3-26

2-Deuterio-2-methyl-1-indanone was then converted to the corresponding allylsilane under the normal reaction conditions previously outlined. This reaction afforded a mixture of isomers in 47 % yield containing mainly the corresponding *E* and *Z*

vinylsilane, as well as the corresponding allylsilane. This result was supported by GC/MS and ^{1}H NMR data. The yield of allylsilane was 19 % and that of vinylsilanes were 26 %; GC/MS data indicated 42 % of the allylsilane was deuteriated. These data strongly suggested deprotonation followed by a 1,5 hydrogen shift was the major pathway in the conversion of 2-methyl-1-indanone to the corresponding allylsilane.

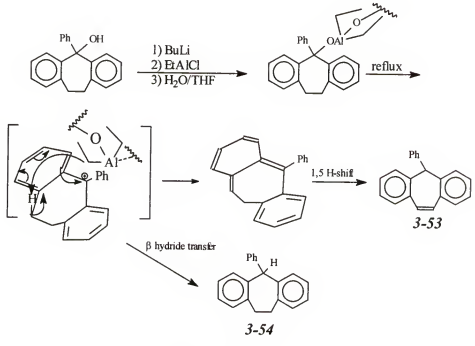
An additional experiment was performed to examine the possibility of benzylic proton abstraction followed by 1,5 hydrogen shift. The alcohol, 5-hydroxy-5-phenyl-10,11-dihydro-5 *H*-dibenzo[*a,d*]cyclohepten ***3-52***,[95] a white solid was prepared by the reaction of dibenzosuberone with phenyl magnesium bromide in 88 % yield (Scheme 3-27).



Scheme 3-27

Mimicking the usual protocol for the preparation of either allyl- or vinyl-silane, the alcohol ***3-52*** previously prepared was then deprotonated by n-butyllithium to generate the corresponding alkoxide anion at 0 °C, diethylaluminum chloride was

introduced followed by addition of 0.1 eq. of water as in shown in Scheme 3-28. Reflux reaction afforded 68 % yield of 5-phenyl-5*H*-dibenzo[*a,d*]cycloheptene[95] ***3-53***, and 20 % yield of 5-phenyl-10,11-dihydro-5*H*-dibenzo[*a,d*]cycloheptene[95] ***3-54***.



Scheme 3-28

As shown above, a straightforward explanation for the transformation of ***3-52*** to ***3-53*** was proposed. The mechanism involves a benzylic cation formation as predicted upon reflux, then abstraction of a benzylic hydrogen producing an intermediate which was then converted to ***3-53*** by a 1,5 hydrogen shift. Similar to the case of 9-xanthone (chapter 2), formation of ***3-54*** provides additional evidence to support our proposed carbocation intermediate elimination (E1 like) mechanism.

Since the literature ^{1}H NMR data on these two compounds were recorded on a 60 M Hz machine and our data were recorded on 300 MHz machine, it was difficult for us to prove the identities of ***3-53*** and ***3-54*** by comparing recorded spectra with the literature

data. To prove their identities, the mixture was reduced by hydrogenation to convert ***3-53*** to ***3-54***, and was purified by flash chromatography with silver nitrate impregnated silica gel. Hydrogenation was done by reacting the product mixture with hydrogen gas in the presence of a catalytic amount of Pd/C (10 mol %) to afford 72 % of reduced product. The disappearance of the vinyl hydrogen peak at δ 6.574 ppm and methine hydrogen peak at 5.368 ppm indicated ***3-53*** had been consumed. Peaks at δ 5.140 (methine hydrogen) and two sets of multiplets (methylene hydrogens exhibits a AA'BB' pattern) at δ 2.648 (m, 2H) and 2.995 (m, 2H) ppm remained unchanged after hydrogenation. This indicated the existence of ***3-54***, whose identity was supported by melting point determination, HRMS and ^{13}C NMR.

Product ***3-53*** was purified by using flash chromatography with silver nitrate impregnated silica gel as stationary phase. It was then characterized by melting point determination, ^{1}H NMR, ^{13}C NMR and HRMS and was determined to be 5-phenyl-5*H*-dibenzo[*a,d*]cycloheptene ***3-53***.

Conclusion

A convenient one-pot synthesis of allylsilanes involving the use of organoaluminate leaving group was developed. This methodology offers a chemoselective and regioselective transformation of enolizable ketones to allylsilanes in fair to good yield. Mechanistic studies were performed on 9-xanthone, 4-phenylcyclohexanone, 2-deuterio-2-methyl-1-indanone, and dibenzosuberone and suggest the reaction proceeds via a syn E1 like elimination.

CHAPTER 4
EXPERIMENTAL

General

Apparatus and Technique

All glassware was flame dried under vacuum and filled with argon gas for air sensitive reactions. Standard syringe techniques were applied for transferring liquid reagents to reaction flasks under an inert atmosphere of argon.

Instrumental Analysis

^{1}H NMR spectra were recorded on Varian VXR-300 (300MHz) or a Gemini-300 (300MHz) with anisole (reference peak at 3.79 ppm, singlet) or TMS or residual CH signals on $CDCl_3$ or C_6D_6 as internal standards. ^{13}C NMR spectra were recorded on Varian VXR-300 (300MHz) or a Gemini-300 (300MHz) with either CH signals on $CDCl_3$ or C_6D_6 as internal standard. A Perkin-Elmer 1600 series FT-IR spectrophotometer was employed to record infrared spectra in wave numbers (cm^{-1}). Sample mass determinations were analyzed by Finnigan MAT GCQ^{TM} GC/MS system and Finnigan MAT 95Q.

Solvents

Xylene was freshly distilled from P_2O_5 in an atmosphere of nitrogen. Hexanes, THF, and diethyl ether were freshly distilled from sodium and benzophenone in an atmosphere of nitrogen before transferring to the reaction vessels. All solvents were transferred by syringes.

Separations

Analytical TLC employed Whatman 4410-222 precoated silica gel plates (0.25 mm) using UV light as an indicator. Microscale purifications were done using Preparative TLC plates on Whatman 4851-810 precoated silica gel plates (1 mm) or Analtech, Inc., alumina GF (250 microns) using UV light as an indicator. Flash chromatography was employed using Kieselgel silica gel 60 (230-400 mesh).

Experimental Procedures

Synthesis of Tris(trimethylsilylmethyl)aluminum lithium bromide complex *2-1*.[54]

In a dry box, aluminum bromide (sublimed, 7.74 g, 0.029 mol) was placed in a flame dried 250 mL round bottom flask equipped with a stir bar and a rubber septum. Outside the dry box, 60 ml of dry, distilled hexanes was introduced into the flask under argon through a rubber septum. The resulting suspension was then stirred and cooled in an ice bath for approximately 10 minutes. Trimethylsilylmethyllithium (90 ml, 0.090 mol) was added dropwise through the septum to the stirred solution. As the injection proceeded, a white precipitate formed in the colorless solution. After injection of the lithium reagent, the resulting mixture was heated under reflux for twelve hours. The

reaction mixture was cooled to room temperature and the solvent was removed by cannula filtration. The remaining white powder was rinsed with three portions (20 ml) of distilled dry hexanes. The remaining solvent was evaporated under vacuum for several hours, and the dried solid was transferred to a dry box and stored in an amber bottle. The yield of the transferred solid was 60 %, 9.54 g. IR (KBr): 2951.9 (s), 2898.7 (w), 2845.4 (w), 2807.3(w), 2362.9 (m), 2342.6 (sh), 1244.4 (s), 1050.3 (vw), 970.2 (m, sh), 936.4 (m, sh), 845.6 (vs), 826.0 (vs), 753.0 (s), 738.8 (sh), 721.0 (sh), 681.8 (m), 667.6 (sh), 580.4 (w).

Reaction of *2-1* with Benzophenone

Benzophenone (0.40 g, 2.20 mmol) and the tris(trimethylsilylmethyl)aluminum lithium bromide complex $[(TMSCH_2)_3Al{\bullet}3LiBr]$ (1.40 g, 2.55 mmol) were placed in a 250 ml dry schlenk flask equipped with a rubber septum, magnetic stir bar, and purged with argon gas. To the greenish yellow solid mixture, 25 ml of distilled hexanes was introduced. The solution mixture was then heated under reflux in argon for 12 hours. After the reflux period, the colorless suspension was cooled to room temperature and quenched with saturated ammonium chloride solution in ice followed by extraction with ether. The combined organic layers were dried (anhydrous magnesium sulfate), filtered, and concentrated in vacuo to yield an oil (0.50 g, 91 % yield) which was analyzed by GC and GC/MS. The crude product mixture consisted of 1,1-diphenylethene ***2-21*** and (2,2-diphenylvinyl)trimethylsilane ***2-20***,[96] in the ratio (GC) of 1 : 18, respectively: ^{1}H NMR (***2-20***) ($CDCl_3$), trimethylsilyl δ -0.13 (s,9H), 6.21 (s, 1H), 7.30 (m, 10H) and a small (singlet) peak at 5.42 representing the olefin (***2-21***) impurity.

General Procedure for Organoaluminum Promoted "Abnormal Peterson Olefination" with Nonenolizable Aromatic Ketones

To a 0.1 M solution of the appropriate ketone in freshly distilled xylene under argon, cooled to 0 °C, was added 1.2 eq. of of 0.5 M $LiCH_2TMS$ in hexanes (Aldrich). The solution was stirred at 0 °C for 15 minutes followed by addition of 1.4 eq. of 1.8 M of Et_2AlCl and, subsequently, 0.1 eq. of a 1 M solution of H_2O in THF was added to the resulting aluminate complexes. The resulting solution was refluxed for 24-48 hours. After reflux, the solution was quenched carefully with 100 mL 0.5 % $NaHCO_3$. The biphasic solution was allowed to react for approximately half an hour (hydrolysis of aluminum complexes) with periodic gentle swirling, without shaking the separatory funnel (shaking the separatory funnel will result in an unbreakable emulsion). As the hydrolysis of the aluminum complex completed the solution stopped bubbling and white precipitate began to settle to the bottom of the aqueous layer. The aqueous layer, with the white precipitate, was drained, the organic layer was washed with two portions of 20 mL of 0.5 % $NaHCO_3$ (normal extraction technique was resumed) and the combined aqueous layers were further extracted with ether. The ether extract was dried over anhydrous $MgSO_4$ for 30 minutes. Solvent was removed in vacuo or by fractional distillation.

Synthesis of (2,2-Diphenylvinyl)trimethylsilane *2-20*

To a 27 mL xylene solution of benzophenone (500 mg, 2.7 mmol) was added 1.2 eq. of $LiCH_2TMS$ (0.5 M in hexanes, 6.6 mL, 3.3 mmol), 1.4 eq. of Et_2AlCl (1 M in hexanes, 3.8 mL, 3.8 mmol), and 0.1 eq. of H_2O (1 M in THF, 0.3 mL, 0.3 mmol). The mixture was refluxed for 24 hours according to the general procedure. After workup, 0.69 g of colorless oil was obtained. ^1H NMR analysis of the crude product showed the presence of ***2-21*** (2 %) and ***2-20*** (71 %) using anisole as the internal standard. A larger

scale reaction was also performed using 4 g (22 mmol) of benzophenone (0.1 M in xylene). Other reagents were scaled up accordingly. The crude product mixture was distilled under reduced pressure at 2 mm Hg and 110 °C to afford an oil (3.48 g, 65 % yield) containing ***2-20*** (91 %) and ***2-21*** (9 %).

Reaction of 4,4'-dimethoxybenzophenone *2-6*

To a 25 mL xylene solution of 4,4'-dimethoxybenzophenone (600 mg, 2.5 mmol) was added 1.2 eq. of $LiCH_2TMS$ (0.5 M in hexanes, 9 mL, 3 mmol), 1.4 eq. of Et_2AlCl (1.8 M in toluene, 1.9 mL, 3.5 mmol), and 0.1 eq. of H_2O (1 M in THF, 0.3 mL, 0.3 mmol). The mixture was refluxed for 24 hours. After workup, the reaction afforded a colorless oil. ^1H NMR spectra and GC/MS analysis of the crude product mixture showed the presence of 2,2-(4,4'-dimethoxyphenyl)vinyltrimethylsilane ***2-8***[97] (57 %, NMR yield; determined by the known amount of acetophenone as internal standard), 1,1-(4,4'-dimethoxyphenyl)ethene ***2-9*** (small trace) and 1,1-(4,4'-dimethoxyphenyl)-2-trimethylsilylethanol ***2-7*** (26 %, NMR yield). A scale up reaction was performed with 4.5 g (19 mmol) of 4,4'-dimethoxybenzophenone (0.1 M in xylene). Other reagents were scaled up accordingly. The product mixture was distilled at 0.01 mm Hg and 152 °C to yield 4.81 g of colorless oil which consisted of ***2-8*** in 83 % and a small trace of ***2-9***. ^1H NMR (***2-8***) ($CDCl_3$) δ -0.06 (s, 9 H), 3.81 (s, 3H), 3.86 (s, 3H), 6.18 (s, 1H), 6.83 (d, J = 9 Hz, 2H), 6.91 (d, J = 9 Hz, 2H), 7.16 (d, J = 9 Hz, 2H), 7.27 (d, J = 9 Hz, 2H). ^{13}C NMR (***2-8***) ($CDCl_3$) δ 0.27, 55.30, 113.24, 113.37, 127.20, 128.58, 130.00, 135.38, 136.44, 156.37, 159.07, 159.36. GC/MS *m/e* (rel intensity) of ***2-8***: 312 (M^+, 46), 297 (47), 282 (12), 165 (100), 73 (6). ***2-9***: 240 (M^+, 100), 225 (82), 209 (43), 165 (40). ***2-7***:

313 (M-17, 26), 165 (16), 73 (100). HRMS (***2-8***) calcd for $C_{19}H_{24}O_2Si$: 312.1546; found: 312.1564.

Reaction of 4,4'-dichlorobenzophenone *2-10*

To a 16 mL xylene solution of 4,4'-dichlorobenzophenone (422 mg, 1.7 mmol) was added with 1.2 eq. of $LiCH_2TMS$ (0.5 M in hexanes, 4.0 mL, 2.0 mmol), 1.4 eq. of Et_2AlCl (1 M in hexanes, 2.3 mL, 2.3 mmol), and 0.1 eq. of H_2O (1 M in THF, 0.2 mL, 0.2 mmol). The solution was refluxed for 22 hours. After workup, most of the solvent was fractionally distilled to afford a colorless oil. ^1H NMR spectra and GC/MS analysis of the crude product mixture showed the presence of 2,2-(4,4'-dichlorophenyl)vinyltrimethylsilane ***2-12*** (75 %, NMR yield; determined by the known amount of anisole as internal standard), 1,1-(4,4'-dichlorophenyl)ethene ***2-13*** (4 %, NMR yield) and 1,1-(4,4'-dichlorophenyl)-2-trimethylsilylethanol ***2-11*** (12 %, NMR yield). A portion of the mixtures was purified by preparative TLC (silica gel) to provide pure ***2-12***: ^1H NMR (***2-12***) ($CDCl_3$) δ -0.11 (s, 9 H), 6.27 (s, 1H), 7.08-7.32 (m, 8H). ^{13}C NMR (***2-12***) ($CDCl_3$) δ -0.03, 128.20, 128.40, 129.43, 130.94, 131.09, 133.56, 133.70, 140.56, 141.29, 154.55. GC/MS *m/e* (rel intensity) of ***2-12***: 320 (M^+, 12), 305 (45), 169 (100), 75 (12). ***2-13***: 248 (M^+, 44.72), 213 (57), 178 (100), 75 (18). ***2-11***. 322 (M-17, 6), 307 (100), 304 (76), 289 (54). HRMS calcd for $C_{17}H_{18}Cl_2Si$ ***2-12***: 320.0555, found: 320.0542.

Reaction of Cyclopropyl Phenyl Ketone *2-14*

To a 36 mL xylene solution of cyclopropyl phenyl ketone (0.5 mL, 3.6 mmol) was added with 1.2 eq. of $LiCH_2TMS$ (0.5 M in hexanes, 8.7 mL, 2.0 mmol), 1.4 eq. of Et_2AlCl (1 M in hexanes, 5.1 mL, 5.1 mmol), and 0.1 eq. of H_2O (1 M in THF, 0.4 mL, 0.4 mmol). The reaction mixture was refluxed for 24 hours. After workup, most of the

solvent was removed by fractional distillation and afforded a colorless oil. ^{1}H NMR and GC/MS analysis of the crude product mixture showed the presence of E and Z isomers of 2-cyclopropyl-2-phenylvinyltrimethylsilane ***2-16*** (78 %, NMR yield). A large scale reaction was performed by using 4 g (27 mmol) of cyclopropyl phenyl ketone (0.1 M in xylene). Amounts of other reagents were scaled up accordingly. The product mixture was distilled at 0.01 mm Hg and 105 °C to afford a colorless oil (4.36 g) which consisted of 68 % yield of ***Z 2-16***, 5 % yield of ***E 2-16*** and 1 % yield of 1-phenyl-1-cyclopropylethene ***2-17***. ^{1}H NMR (***Z-2-16***) ($CDCl_3$) δ -0.21 (s, 9 H), 0.48 (m, 2H), 0.69 (m, 2H), 1.68 (m, 1H), 5.56 (s, 1H), 7.12-7.30 (m, 5H). ^{13}C NMR (***Z-2-16***) ($CDCl_3$) 0.09, 6.33, 21.319, 124.06, 126.94, 127.58, 128.82, 142.12, 160.39. NOE, irradiation at 5.56 ppm (vinyl proton) enhanced the signal at 1.68 ppm (cyclopropyl proton) by 4 % indicating the major isomer was Z-2-cyclopropyl-2-phenylvinyltrimethylsilane (74 %). GC/MS *m/e* (rel intensity) of ***Z-2-16***: 216 (M^+, 8), 201 (100), 73 (22). ***E-2-16***: 216 (M^+, 13), 201 (100), 73 (32). HRMS calcd for $C_{14}H_{20}Si$ ***2-16***: 216.1334, found: 216.1385.

Reaction of 9-fluorenone *2-34*

To a 28 mL xylene solution, 9-fluorenone (0.5 g, 2.8 mmol) was added 1.2 eq. of $LiCH_2TMS$ (0.5 M in hexanes, 6.6 mL, 3.3 mmol), 1.4 eq. of Et_2AlCl (1.8 M in toluene, 2.2 mL, 3.8 mmol), and 0.1 eq. of H_2O (1 M in THF, 0.3 mL, 0.3 mmol) were added to the reaction mixture which was refluxed for 48 hours. After reflux, the resulting orange solution was washed with 100 mL of a 0.5 % $NaCO_3$ solution prepared from oven dried $NaHCO_3$ and freshly distilled H_2O. The aqueous layer was extracted by 3 portions of 15 mL freshly distilled CH_2Cl_2. The organic layer was dried over anhydrous $NaHCO_3$. Most of the solvent was removed by vacuum distillation to afford a yellow oil. All reaction

procedures including workup and separation were done in an argon atmosphere. ^{1}H NMR spectra and GC/MS analysis of the crude product mixture showed the presence of 2-(9-fluorenyl)vinyltrimethylsilane ***2-35*** (33 %, NMR yield; determined by known amount of anisole as internal standard) and 9-(trimethylsilylmethyl)fluoren-9-ol ***3-37*** (40 %, isolated yield). Attempted purification of ***2-35*** (conducted under argon) led to a white pasty solid by flash choromatography (alumina). ^{1}H NMR (***2-35***) ($CDCl_3$) δ -0.61 (s, 9 H), 6.07 (s, 1H), 7.09-7.7 (m, 8H). MS (EI) ***m/e*** of the polymer: 178, 250, and 354 indicated the presence of monomeric units of ***2-35*** and ***2-36*** as well as a dimeric unit of ***2-36***. HRMS (***2-35***) calcd for $C_{17}H_{18}Si$: 250.1178, found: 250.1184.

Reaction of dibenzosuberone *2-26*

A xylene solution (24 mL) of dibenzosuberone (500 mg, 2.4 mmol) was treated with 1.2 eq. of $LiCH_2TMS$ (0.5 M in hexanes, 5.8 mL, 2.9 mmol), 1.4 eq. of Et_2AlCl (1.8 M in toluene, 1.8 mL, 3.4 mmol), and 0.1 eq. of H_2O (1 M in THF, 0.2 mL, 0.2 mmol). The mixture was refluxed for 24 hours. After workup, most of the solvent was removed by fractional distillation to afford a colorless oil. ^{1}H NMR and GC/MS analysis of the crude product mixture showed the presence of 10,11-dihydro-5*H*-dibenzo[*a,d*]cyclohepten-5-ylidenmethyltrimethylsilane ***2-28*** (64 %, NMR yield; determined by known amount of anisole as internal standard) and 5-methylidene-10,11-dihydro-5*H*-dibenzo[*a,d*]cycloheptene ***2-29*** (4 %, NMR yield). A large scale reaction with 4.5 g (22 mmol) of dibenzosuberone ***2-20*** was performed. Amounts of other reagents were scaled up accordingly. The product mixture was distilled at 0.1 mm Hg and 120 °C to afford an oil (4.44 g) which corresponds to a 65 % yield of ***2-28*** and 11 % yield of ***2-29***. ^{1}H NMR (***2-28***) ($CDCl_3$) δ -0.12 (s, 9 H), 3.15 (br, 4H), 6.04 (s, 1H), 7.03-7.37

(m, 8H). ^{13}C NMR (***2-28***) ($CDCl_3$) δ -0.15, 31.82, 33.93, 125.72, 126.05,126.19, 127.26, 127.34, 127.89, 128.18, 130.09, 133.23, 136.13, 138.83, 143.20, 143.35, 159.77. GC/MS *m/e* (rel intensity) of ***2.28***: 278 (M^+, 17), 263 (100). ***2-29***: 206 (M^+, 100), 205 (86), 191 (40). HRMS (***2-28***) calcd for $C_{19}H_{22}Si$: 278.1491; found: 278.1491.

Preparation of 2,2-dimethyl-1-indanone *2-22*[57]

To a 20 mL THF solution of 1-indanone (1.5 g, 11 mmol) was added 6 eq. of *t*-BuOK (68 mL, 1 M, 68 mmol) and 6 eq. of MeI (4.24 mL, 68 mmol) at –78 °C. After the mixture had been refluxed overnight, a purple solution was quenched with 5 % HCl and was extracted with ether. The ether solution was dried with anhydrous $MgSO_4$ for half an hour. After solvent evaporation, a red oil was isolated in 0.95 g, 54 % yield. ^{1}H NMR (***2-22***) ($CDCl_3$) δ 1.189 (s, 6 H), 2.954 (s, 2 H), 7.510 (m. 4 H). ^{13}C NMR (***2-22***) ($CDCl_3$) δ 25.067, 42.656, 45.267, 124.198, 126.490, 127.233, 134.685, 135.110, 152.077, 211.248.

Reaction of 2,2-dimethyl-1-indanone *2-22*

To a 31 mL xylene solution of 2,2-dimethyl-1-indanone (500 mg, 3.1 mmol) was added 1.2 eq. of $LiCH_2TMS$ (0.7 M in hexanes, 5.4 mL, 3.8 mmol), 1.4 eq. of Et_2AlCl (1.8 M in toluene, 2.43 mL, 4.37 mmol), and 0.1 eq. of H_2O (1 M in THF, 0.3 mL, 0.3 mmol). The mixture was refluxed for 24 hours. After workup, the product mixture was distilled at 0.03 mm Hg and 36 °C to afford a colorless oil (0.44 g) in 61 % yield. ^{1}H NMR (***Z 2-24***) ($CDCl_3$) δ 0.333 (s, 9 H), 1.249 (s, 6 H), 2.894 (s, 2 H), 5.563 (s, 1 H), 7.282 (m, 4 H). ^{13}C NMR (***Z 2-24***) ($CDCl_3$) δ 0.330, 29.392, 45.236, 46.587, 116.989, 124.684, 125.442, 125.943, 128.311, 140.573, 145.126, 168.072. NOE: irradiation at 5.56 ppm (vinyl protons) enhanced the signal at 1.249 ppm (methyl proton) by 3 % indicating that the major isomer was the *Z*-1-(1-trimethylsilylmethylidene)-2,2-dimethyl-3,3-

dihydro-1*H*-indene ***Z 2-24*** (98 %). GC/MS *m/e* (rel intensity) of ***Z 2.24***: 230 (M^+, 65), 215 (90), 73 (100). HRMS (***2-24***) calcd for $C_{15}H_{22}Si$: 230.1491, found: 230.1490.

Reaction of 4-phenyl-2'-methylbenzophenone *2-30*

To a 22 mL xylene solution of 4-phenyl-2'-methylbenzophenone (600 mg, 2.2 mmol) was added 1.2 eq. of $LiCH_2TMS$ (0.5 M in hexanes, 5.3 mL, 2.7 mmol), 1.4 eq. of Et_2AlCl (1.8 M in toluene, 1.7 mL, 3.1 mmol), and 0.1 eq. of H_2O (1 M in THF, 0.2 mL, 0.2 mmol). The mixture was refluxed for 24 hours. After workup, most of the solvent was removed by fractional distillation to afford a colorless oil. ^1H NMR and GC/MS analysis of the crude product mixture showed the presence of E and Z isomers of [2-(4-biphenyl)-2-(o-tolyl)vinyl]trimethylsilane ***2-32*** (78 %, NMR yield; determined by known amount of anisole as internal standard) and [1-(4-biphenyl)-1-(o-tolyl)ethene ***2-33*** (7 %, NMR yield). A portion of the mixtures was purified by preparative TLC (silica gel) to afford pure ***2-32*** ^1H NMR (***Z-2-32***) ($CDCl_3$) δ -0.12 (s, 9 H), 2.08 (s, 3H), 6.50 (s, 1H), 7.17-7.58 (m, 13H). NMR (***E-2-32***) ($CDCl_3$) δ 0.05 (s, 9 H), 2.16 (s, 3H), 5.84 (s, 1H), 7.17-7.58 (m, 13H). ^{13}C NMR (isomers of ***2-32***) ($CDCl_3$) δ -0.46, 0.41, 19.71, 20.59, 125.37,125.50, 125.72, 126.64. 126.92, 127.25, 127.60, 128.72, 128.93, 129.27, 129.48, 129.90, 130.09, 130.28, 130.39, 133.18, 135.08, 136.28, 140.04, 140.25, 140.63, 140.74, 141.48, 142.08, 145.60, 155.78, 158.12. NOE, irradiation at 2.16 ppm (methyl protons) enhanced the signal at 5.84 ppm (vinyl proton) by 5 % indicating that the major isomer was the E-[2-(4-phenyl)phenyl-2-(2'-methyl)phenylvinyl]trimethylsilane (52 %, NMR yield) and the Z-isomer was the minor isomer (26 %, NMR yield). GC/MS *m/e* (rel intensity) of ***2-32***: 342 (M^+, 2), 327 (1), 256 (21), 255 (100), 211 (30), 73 (8). ***2-33***: 270

(M^+, 26), 255 (100), 240 (21), 178 (16). HRMS (***2-32***) calcd for $C_{19}H_{22}Si$: 342.1804; found: 342.1791.

Reaction of Xanthone *2-38*

To a 30 mL xylene solution of xanthone (600 mg, 3.1 mmol) was added 1.2 eq. of $LiCH_2TMS$ (0.5 M in hexanes, 7.4 mL, 3.7 mmol), 1.4 eq. of Et_2AlCl (1.8 M in toluene, 2.4 mL, 4.3 mmol), and 0.1 eq. of H_2O (1 M in THF, 0.3 mL, 0.3 mmol). The reaction mixture was refluxed for 24 hours. After workup, most of the solvent was removed by fractional distillation to afford a slightly yellow oil. ^1H NMR analysis of the crude product mixture showed the presence of 9*H*-9-xanthenylidenemethyltrimethylsilane ***2-39*** (52 %, NMR yield; determined by known amount of anisole as internal standard). In addition ^1H NMR and GC/MS analysis of the crude product mixture showed the presence of 9-methylidene-9*H*-xanthene ***2-40*** (2 %, NMR yield) and 9-trimethylsilylmethyl-9-ethyl-9*H*-xanthene ***2-41*** (25 %, NMR yield) . A portion of the mixtures was purified by preparative TLC (silica gel) to afford pure ***2-41***. After purification , the vinyl proton signals of ***2-39*** and ***2-40*** were replaced by multiple vinyl proton signals indicating the alkenes either polymerized or decomposed. ^1H NMR (***2-41***) ($CDCl_3$) δ -0.48 (s, 9 H), 0.51 (t, J = 7.2 Hz, 3H), 1.51 (s, 2H), 2.06 (q, J = 7.2 Hz, 2H), 7.01-7.34 (m, 8H). ^{13}C NMR (***2-41***) ($CDCl_3$) δ -0.76, 9.58, 35.79, 40.08, 42.64, 115.97, 122.80, 126.26, 127.16, 127.37, 150.97. GC/MS *m/e* (rel intensity) of ***2-41***: 281 (M-15, 17), 267 (M-29, 84), 209 (M-87, 54), 73 (100). ***2-40***: 194 (M^+, 100), 165 (44). HRMS (***2-41***) calcd for $C_{18}H_{22}OSi$ (M-29): 267.1205; found: 267.1237.

Preliminary Studies: General Procedures for Organoaluminum Promoted "Abnormal Peterson Olefination" in Allylsilane Syntheses (without $CeCl_3$)

To a 0.1 M solution of the appropriate ketone in xylene under argon and cooled to -78 °C was added 1.2 eq. of a 0.5 M solution of $LiCH_2TMS$ in hexanes (Aldrich). The solution was stirred at 0 °C for 60 minutes followed by addition of 1.4 eq. of 1.8 M of Et_2AlCl. To the aluminate complex was added 0.1 eq. of a 1 M solution of H_2O in THF. The resulting mixture was refluxed overnight and the solution was quenched with 100 mL of 0.5 % $NaHCO_3$ and the aqueous layer was extracted by 3 portions of 15 mL of CH_2Cl_2. The combined organic extracts were dried over anhydrous $MgSO_4$ for half an hour. Solvent was removed in vacuo or by fractional distillation.

Reaction of acetophenone *3-3*

To a 26 mL xylene solution of acetophenone (0.3 mL, 2.6 mmol) was added 1.2 eq. of $LiCH_2TMS$ (0.5 M in hexanes, 5.2 mL, 3.1mmol), 1.4 eq. of Et_2AlCl (1 M in hexanes, 3.6 mL, 3.6 mmol), and 0.1 eq. of H_2O (1 M in THF, 0.4 mL, 0.4 mmol) and was refluxed for 24 hours. After workup, the solvent was removed to afford a slightly yellow oil ***3-4*** (17 %, NMR yield; determined by known amount of anisole as internal standard). ^1H NMR ($CDCl_3$) δ -0.07 (s, 9H), 2.05 (s, 2H), 4.90 (s, 1H), 5.20 (s, 1H), 7.35 (m, 5H).

Reaction of 2-acetonaphthone *3-7*

To a 30 mL xylene solution of 2-acetonaphthone (500 mg, 2.9 mmol) was added 1.2 eq. of $LiCH_2TMS$ (0.5 M in hexanes, 7.1 mL, 3.5 mmol), 1.4 eq. of Et_2AlCl (1M in hexanes, 4.1 mL, 4.1 mmol), and 0.1 eq. of H_2O (1 M in THF, 0.3 mL, 0.3 mmol). The reaction mixture was refluxed for 29 hours. After workup, most of the solvent was removed to afford a slightly yellow oil. ^1H NMR and GC/MS analysis of the crude

product mixture showed the presence of 2-(1-trimethylsilylmethyl-1-ethenyl)naphthalene ***3-8*** (65 %, NMR yield; determined by known amount of anisole as internal standard), 2-(1-methyl-1-ethenyl)naphthalene ***3-9*** (8 %, NMR yield) , and E and Z isomers of 2-(2-trimethylsilyl-1-methyl-1-ethenyl)naphthalene ***3-10*** (3 %, NMR yield). A portion of the mixtures was purified by preparation TLC (silica gel) to afford pure ***3-8***. ^{1}H NMR (***3-8***) ($CDCl_3$) δ -0.08 (s, 9 H), 2.14 (s, 2H), 4.97 (s, 1H), 5.28 (s, 1H), 7.42-7.80 (m, 7H). ^{13}C NMR (***3-8***) ($CDCl_3$) δ -0.12, 26.15, 110.83, 125.00, 125.77, 126.09, 127.60, 127.70, 128.25, 132.73, 133.27, 139.86, 146.28. GC/MS *m/e* (rel intensity) of ***3-8***: 240 (M^+, 20), 185 (6), 165 (14), 73 (100). ***3-9***: 168 (M^+, 100), 153 (50), 128 (25). ***3-10a***: 240 (M^+, 21), 225 (69), 185 (100), 167 (20), 73 (42). ***3-10b***: 240 (M^+, 22), 225 (53), 185 (100), 167 (13.51), 73 (75.21). HRMS (***3-8***) calcd for $C_{16}H_{20}Si$: 240.1334; found: 240.1331.

Reaction of 1-indanone *3-11*

To a 30 mL xylene solution of 1-indanone (400 mg, 3.0 mmol) was added 1.2 eq. of $LiCH_2TMS$ (0.5 M in hexanes, 7.3 mL, 3.6 mmol), 1.4 eq. of Et_2AlCl (1M in hexanes, 4.3 mL, 4.3 mmol), and 0.1 eq. of H_2O (1 M in THF, 0.3 mL, 0.3 mmol). The resulting mixture was refluxed for 24 hours. After workup, most of the solvent was fractionally distilled and afforded a red oil. ^{1}H NMR and GC/MS analysis of the crude product mixture showed the presence of 3*H*-inden-1-ylmethyltrimethylsilane ***3-12*** (53 %, NMR yield; determined by known amount of anisole as internal stnadard), 1-methylidene-2,3-dihydro-1*H*-indene ***3-13*** (small trace), and 1-(1-trimethylsilylmethylidene)-2,3-dihydro-1*H*-indene ***3-14*** (small trace). A portion of the mixtures was purified by preparative TLC (silica gel) to afford pure ***3-12***.[87] ^{1}H NMR (***3-12***) ($CDCl_3$) δ 0.08 (s, 9 H), 2.08 (s, 2H), 3.37 (s, 2H), 6.06 (s, 1H), 7.22-7.49 (m, 4H). ^{13}C NMR (***3-12***) ($CDCl_3$) δ -0.12, 17.53,

37.65, 119.21, 123.44, 124.14, 125.74, 125.83, 141.55, 144.39, 146.19. GC/MS *m/e* (rel intensity) of ***3-12***: 202 (M^+, 39), 187 (19), 128 (39), 73 (100). ***3-13***: 130 (M+1, 100), 129 (M^+, 87), 115 (71). ***3-14***: 202 (M^+, 67.02), 187 (100), 171 (60), 73 (6). HRMS (***3-12***) calcd for $C_{13}H_{18}Si$: 202.1178; found: 202.1170.

Reaction of 1-(4-chlorophenyl)ethanone *3-15*

To a 30 mL xylene solution of 1-(4-chlorophenyl)ethanone (0.4 mL, 3.1 mmol) was added 1.2 eq. of $LiCH_2TMS$ (7.4 mL, 3.7 mmol), 1.4 eq. of Et_2AlCl (1M in hexanes, 4.3 mL, 4.3 mmol), and 0.1 eq. of H_2O (1 M in THF, 0.3 mL, 0.3 mmol). The reaction mixture was refluxed for 24 hours. After workup, most of the solvents were removed by fractional distillation to afford a slightly yellow oil. ^1H NMR and GC/MS analysis of the crude product mixture indicated the presence of 2-(4-chlorophenyl)allylsilane ***3-16*** (55 % NMR yield; determined by known amount of anisole as internal standard), 2-(4-chlorophenyl)propene ***3-17*** (small trace) , and 2-(4-chloropheny)-2-methylvinylsilane ***3-18*** (2 %, NMR yield). A portion of the product mixture was purified by preparative TLC (silica gel) to isolate ***3-16***. ^1H NMR (***3-16***) ($CDCl_3$) δ -0.07 (s, 9 H), 2.01 (s, 2H), 4.90 (s, 1H), 5.14 (s, 1H), 7.27-7.37 (m, 4H). ^{13}C NMR (***3-16***) ($CDCl_3$) δ -0.14, 26.12, 110.66, 127.66, 128.26, 132.98, 141.27, 145.52. GC/MS *m/e* (rel intensity) of ***3-16***: 224 (M^+, 6), 209 (34), 169 (100), 73 (14). ***317***: 152 (M^+, 94), 137 (24), 117 (100). ***3-18***: 224 (M^+, 6), 209 (100), 169 (39), 73 (12). HRMS (***3-16***) calcd for $C_{12}H_{17}ClSi$: 224.0788, found: 240.0824.

Reaction of 1-adamantyl methyl ketone *3-19*

To a 28 mL xylene solution of 1-adamantyl methyl ketone (500 mg, 2.8 mmol) was added 1.2 eq. of $LiCH_2TMS$ (0.5 M in hexanes, 6.7 mL, 3.4 mmol), 1.4 eq. of

Et_2AlCl (1M in hexanes, 3.9 mL, 3.9 mmol), and 0.1 eq. of H_2O (1 M in THF, 0.3 mL, 0.3 mmol). The resulting mixture was refluxed for 74 hours. After workup, most of the solvent was removed by fractional distillation to afford a colorless oil. ^1H NMR spectra and GC/MS of the crude product mixture showed the presence of [2-(1-adamantyl)allyl]trimethylsilane ***3-20*** (53 %, NMR yield; determined by known amount of anisole as internal standard), [2-(1-adamantyl)methyl]vinyltrimethylsilane ***3-22*** (40 %, NMR yield) and 1-adamantyl-1-methylethene ***3-21*** (2 %, NMR yield). The mixture was purified by flash chromatography (silica gel). ^1H NMR (***3-20 mixture***) ($CDCl_3$) δ 0.058 (s, 9 H, ***3-20*** TMS), 0.120 (s, 9H, ***3-22*** TMS), 1.524-2.022 (m, 18H, ***3-20***, ***3-22***), 4.587 (s, 1H, ***3-20***), 4.705 (s, 1H, ***3-20***), 4.709 (s, 1H, ***3-22***) 5.224 (s, 1H, ***3-22***). ^{13}C NMR (***3-20 mixture***) (APT) ($CDCl_3$) δ -0.41 (down, ***3-20***), 0.27 (down, ***3-22***), 17.37 (down, ***3-22***), 19.71 (up, ***3-20***), 28.73 (down, ***3-20***), 28.88 (down, ***3-22***), 37.00 (up, ***3-20***), 37.30 (up, ***3-22***), 37.72 (up, ***3-22***), 38.07 (up, ***3-20***), 39.52 (up, ***3-22***), 40.87 (up, ***3-20***), 105.51 (up, ***3-20***), 118.75 (down, ***3-22***), 115.95 (up, ***3-20***), 163.43 (up, ***3-22***). GC/MS *m/e* (rel intensity) of ***3-22***: 248 (M^+, 15), 233 (78), 135 (31), 73 (100). ***3-20***: 248 (M^+, 15), 233 (24), 73 (100). ***3-21***[15]: 176 (M^+, 65), 135 (55), 119 (39), 105 (46), 91 (100). HRMS (***3-20***) calcd for $C_{16}H_{28}Si$: 248.1960; found: 248.1938.

Dehydration of Cerium Chloride Heptahydrate

Cerium chloride heptahydrate (10 g) was transferred into a 100 mL round bottom flask and was dehydrated under vacuum (0.02 mm Hg) and at 150 °C for 12 hrs. The compound was stored in a desiccator in a dry box for future use.

General Procedures for [(Trimethylsilyl)methyl]lithium/Cerium Chloride incorporated Organoaluminums Promoted "Abnormal Peterson Olefination" in Allylsilane Synthesis

To a 100 mL schlenk flask equipped with a magnetic stir bar was added dehydrated $CeCl_3$ (1.5 eq. of) and 10 mL of freshly distilled THF. After being stirred for one hour at room temperature, the slurry was cooled to –78 °C and $LiCH_2TMS$ (1.5 eq. of) was introduced. After 30 min of stirring at –78 °C, an enolizable ketone (1 eq. of) was introduced directly to the reaction mixture. The resulting mixture was allowed to stir at –78 °C for 5 hr. After the alkylation step had completed, the reaction mixture was removed from the dry ice/acetone bath. To the reaction mixture, 1.4 eq. of Et_2AlCl, 0.1 eq. of H_2O (1 M in THF), and xylene (dilute the ketone solution to 0.1 M) were introduced successively to the system. The system was purged with argon gas at elevated temperature to remove THF. After the majority of THF had evaporated, the reaction mixture was allowed to reflux for 24 to 96 hr under argon atmosphere. To workup the reaction, 2 spatulas of celite were added to the resulting mixture in open atmosphere. After the resulting mixture had been stirred for 15 min., it was filtered through a celite bed and washed with ether. In a separatory funnel, 100 ml of 0.5 % of $NaHCO_3$ was added slowly to the filtrate without agitating. The biphasic solution was allowed to react for half an hour without stirring. After 30 minutes, white precipitate had settled on the bottom of the aqueous layer. The aqueous layer was then drained and extraction was performed. The combined ether solution was dried over $MgSO_4$ for half an hour. After the solvent had been evaporated, the product mixture was characterized and then further purified.

Reaction of 2-acetonaphthone *3-7*

2-Acetonaphthone (400 mg, 2.4 mmol) was subjected to the reaction conditions described in the general procedure. The reaction mixture was refluxed for 36 hr. GC/MS, ^{1}H and ^{13}C NMR data indicated ***3-8*** as the major product with small traces of ***3-9*** and ***3-10***. Yield was determined by ^{1}H NMR with a known amount of anisole as an internal standard. The reaction afforded 2-(1-trimethylsilylmethyl-1-ethenyl)naphthalene ***3-8*** in 78 %. Spectroscopic data were reported in the preliminary study section.

Reaction of 1-indanone *3-11*

1-Indanone (400 mg, 2.3 mmol) was subjected to the reaction conditions described in the general procedure. The resulting mixture was refluxed for 24 hours. The reaction afforded (3*H*-inden-1-ylmethyl)trimethylsilane ***3-12*** in 75 % (yield determined by ^{1}H NMR with a known amount of anisole as an internal standard). Spectroscopic data were reported in the preliminary study section.

Reaction of 1-(4-chlorophenyl)ethanone *3-15*

1-(4-Chlorophenyl)ethanone (0.4 mL, 3.1 mmol) was subjected to the reaction conditions described in the general procedure. The reaction mixture was refluxed for 36 hours. After workup had been completed, the product mixture was distilled at 72 °C, 0.03 mm Hg to afford a mixture (665 mg, 70 % yield) of 2-(4-chlorophenyl)allylsilane ***3-16*** and 2-(4-chlorophenyl)propene ***3-17*** in 6:1 ratio, respectively, as determined by ^{1}H NMR. This corresponds to a 60 % yield of ***3-16*** and a 10 % yield of ***3-17***. Spectroscopic data were reported in the preliminary study section.

Reaction of 1-adamantyl methyl ketone *3-19*

1-Adamantyl methyl ketone (500 mg, 2.8 mmol) was subjected to the reaction conditions described in the general procedure. The resulting mixture was refluxed for 4 days. After workup had been completed, the product mixture was distilled at 0.03 mm Hg and 150 °C. The reaction afforded a mixture (332 mg) of [2-(1-adamantyl)allyl]trimethylsilane ***3-20*** and [2-(1-adamantyl)methyl]vinyltrimethylsilane ***3-22*** in a 7:1 ratio, respectively, as determined by ^{1}H NMR. This corresponds to a 42 % yield of ***3-20*** and a 6 % yield of ***3-22***. ^{1}H NMR (***3-20***) ($CDCl_3$) δ 0.058 (s, 9 H), 1.26-2.00 (m, 18H), 4.587 (s, 1H), 4.705 (s, 1H). ^{13}C NMR (***3-20***) (APT) ($CDCl_3$) δ -0.459 (down) , 19.694 (up), 28.694 (down), 36.996 (up), 40.866 (up), 105.501 (up), 155.947 (up). A "quantitative" ^{13}C experiment was used to establish the relationship between integrated peak areas and the number of nuclei under those areas. To perform this experiment, the instrument was set to allow ten seconds between pulses for relaxation, with decoupling only during the acquisition. The resulting spectrum showed the overall peak areas of ***3-20*** were much greater than ***3-22***; therefore, this strongly suggests ***3-20*** was the major compound of the reaction. Other spectroscopic data were reported in the preliminary study section.

Reaction of 1,3-diphenyl-2-propanone *3-23*

1,3-Diphenyl-2-propanone (500 mg, 2.4 mmol) was subjected to the reaction conditions described in the general procedure. The resulting mixture was refluxed for 36 hours. The product mixture was distilled at 173 °C, 0.25 mm Hg to afforded (498 mg) of *Z*-2-benzyl-3-phenylallyltrimethylsilane ***3-24Z*** and *E*-2-benzyl-3-phenylallyltrimethylsilane ***3-24E*** in a 3:1 ratio, respectively, as determined by ^{1}H NMR.

This corresponds to a 56 % yield of ***3-24Z*** and a 18 % yield of ***3-24E***. ^{1}H NMR (***3-24 mixture***) ($CDCl_3$) δ 0.133 (s, 9 H, ***3-24Z***, TMS), 0.191 (s, 9H, ***3.24E***, TMS), 1.709 (s, 2H, ***3-24E***, CH_2), 1.943 (s, 2H, ***3-24Z***, CH_2), 3.541 (s, 2H, ***3-24Z***, CH_2), 3.706 (s, 2H, ***3-24E***, CH_2), 6.326 (s,1H, ***3-24Z***, C=C**H**), 6.490 (s, 1H, ***3-24E***, C=C**H**), 7.287 (m, 20 H, ***3-24Z*** and ***E***, aromatic). ^{13}C NMR (***3-24 mixture***) ($CDCl_3$) δ -1.88, -1.051, 21.546, 27.541, 46.768, 48.408, 124.380, 125.169, 125.442, 125.685, 125.852, 125.958, 126.140, 126.368, 126.656, 127.264, 128.022, 128.159, 128.295, 128.356, 128.599, 128.781, 129.100, 129.343, 129.601, 130.830, 130.644, 138.615, 138.955, 139.071, 139.465, 139.647, 139.905, 140.543. 155.855. NOE: irradiation at δ 6.326 and δ 6.490 enhanced the signal at δ 3.541 and δ 1.709, respectively by 3 %. These results indicated the *Z*-isomer as the major isomer. GC/MS ***m/e*** (rel intensity) of ***3-24E***: 265 (M-15, 19), 206 (28), 135 (77), 73 (100). ***3-24Z***: 280 (M^+, 7), 265 (10), 73 (100). ***3-26***: 280 (M^+, 1), 265 (3), 73 (100). HRMS (***3-20***) calcd for $C_{19}H_{24}Si$: 280.1647; found: 280.1645.

4-Phenylcyclohexanone *3-27*

4-Phenylcyclohexanone (500 mg, 2.9 mmol) was subjected to the reaction conditions described in general procedure. The resulting mixture was refluxed for 48 hours. After workup and solvent evaporation, this reaction afforded a mixture (581 mg) of 4-phenyl-1-(trimethylsilylmethyl)-1-cyclohexene ***3-28*** and 4-phenyl-1-(trimethylsilylmethylene)cyclohexane ***3-30*** in a ratio of 1:1.3, respectively, as determined by ^{1}H NMR. This corresponds to a 34 % yield of ***3-28*** and a 45 % yield of ***3-30***. ^{1}H NMR (***3-30 mixture***) ($CDCl_3$) δ 0.032 (s, 9 H, ***3-30***), 0.103 (s, 9H, ***3-28***), 1.608-2.743 (m, 17H, ***3-28***, ***3-30***), 5.20 (s, 1H, ***3-30***), 5.300 (br, 1H, ***3-28***), 7.147-7.307 (m, 10H, ***3-28***, ***3-30***). ^{13}C NMR (***3-30 mixture***) ($CDCl_3$) δ -1.127, -0.300, 27.708, 29.726, 30.303, 31.638,

33.687, 34.112, 35.615, 36.009, 40.092, 44.159, 118.477, 121.481, 125.837, 125.989, 126.839, 126.265, 128.326, 135.383, 146.735, 147.372, 158.496. Lit. ^{1}H NMR (***3-28***)[79] (300 M Hz, $CDCl_3$) δ 0.01 (s, 9H), 1.44 (s, 2H), 1.66-1.83 (m, 1 H), 1.83-2.00 (m, 2H), 2.05-2.33 (m, 3H), 2.66-2.77 (m, 1H), 5.28 (br, 1H), 7.17-7.32 (m, 5H). GC/MS *m/e* (rel intensity) of ***3-28***: 244 (M^+, 14), 229 (41), 170 (90), 73 (100). HRMS (***3-28***) calcd for $C_{16}H_{24}Si$: 244.1647; found: 244.1648.

Preparation of 4-phenyl-1-trimethylsilylmethylcyclohexan-1-ol *3-31*

To a 100 mL schlenk flask equipped with a magnetic stir bar was added dehydrated $CeCl_3$ (412 mg, 1.7 mmol, 1.5 eq. of) and 5 mL of freshly distilled THF. After stirring for one hour at room temperature, the slurry was cooled to –78 °C and $LiCH_2TMS$ (3.44 mL, 1.7 mmol, 1.5 eq. of) was introduced. After 30 min of stirring at –78 °C, 4-phenylcyclohexanone ***3-27*** (200 mg, 1.1 mmol, 1 eq. of) was introduced directly to the reaction mixture. The resulting mixture was allowed to stir at –78 °C for 5 hr. To workup the reaction, 2 spatulas of celite was added to the resulting mixture in open atmosphere. After the resulting mixture had been stirred for 15 min, it was filtered through a celite bed and was washed with ether. The ether solution was washed with 3 portions of 25 ml of 0.5 % of $NaHCO_3$. The combined ether layers were dried over $MgSO_4$ for half an hour. After solvent evaporation, 1-(trimethylsilylmethyl)-4-phenylcyclohexanol ***3-31*** (282 mg), an oil, was isolated in 98 % yield. ^{1}H NMR (***3-31***)[85] (C_6D_6) δ 0.075 (s, 9 H), 0.827 (s, 2H), 1.280-2.316 (m, 10H), 7.080-7.219 (m, 5H). ^{13}C NMR (***3-31***) (C_6D_6) δ 0.815, 30.119, 35.081, 40.787, 44.156, 71.001, 126.240, 127.169, 128.653, 147.683. HRMS (***3-31***) calcd for $C_{16}H_{26}SiO$: 262.1753; found: 244.1592 (M-18).

Reaction of 4-phenyl-1-trimethylsilylmethylcyclohexan-1-ol *3-31*

To a 10 mL solution of acetonitrile in a 25 mL round bottom flask, ***3-31*** (213mg, 0.8 mmol) and 18 drops of 10 % HF in acetonitrile were added successively. The reaction was stirred for 12 hr at room temperature. Workup was performed by transferring the resulting mixture into 10 mL of 10 % $NaHCO_3$ and then extracted by pentane. The pentane solution was dried over anhydrous $MgSO_4$ for half an hour. Solvent evaporation afforded 1-methylene-4-phenylcyclohexane ***3-29*** (81.3 mg) in 59 % yield. ^{1}H NMR (***3-29***) ($CDCl_3$) δ 1.218 –2.673 (m, 9 H), 4.637 (s, 2H), 7.108-7.266 (m, 5H). ^{13}C NMR (***3-29***) ($CDCl_3$) δ 35.129, 35.493, 44.128, 107.337, 125.958, 126.808, 128.311, 146.826, 148.753. Lit. ^{1}H NMR (***3-29***)[90] ($CDCl_3$, 300 M Hz), δ 1.20-2.87 (m, 9H), 4.54 (s, 2H), and 7.18 (s, 5 H).

Tetralone *3-32*

Tetralone (0.5 mL, 3.8 mmol) was subjected to the reaction conditions described in the general procedure. The resulting mixture was refluxed for 41 hours. After workup and solvent evaporation, distillation at 62 °C, 0.25 mm Hg and further purification by flash chromatography to afforded a mixture (497 mg) of (3,4-dihydronaphthalen-1-ylmethyl)trimethylsilane ***3-33***,[87] *E/Z* (1-trimethylsilylmethylene)-1,2,3,4-tetrahydronapthalene ***3-35***, and small trace of 1-naphthylmethyltrimethylsilane in a 3.4:1 ratio, respectively, as determined by ^{1}NMR. This corresponds to a 47 % yield of ***3-33*** and a 14 % yield of ***3-35***. ^{1}H NMR (***3-33 mixture***) ($CDCl_3$) δ 0.029 (s, 9 H, ***3-33***), 0.189 (s, 9H, ***3-35***), 0.255 (s, 9H, ***3-35***) 1.102-3.028 (m, 18H, ***3-33***, ***3-35***), 5.536 (s, 1H, ***3-35***), 5.741 (t, J = 4.2 Hz, 1H, ***3-33***), 6.149 (s, 1 H, ***3-35***), 7.163-8.121 (m, 12H, ***3-33, 3-35***). ^{13}C NMR (***3-33 mixture***) ($CDCl_3$) δ -1.066, -0.133, 0.664, 22.351, 23.261, 23.823,

24.217, 28.952, 29.711, 30.348, 32.124, 37.982, 122.058, 122.726, 123.394, 124.805, 125.154, 125.943, 126.368, 126.611, 127.264, 127.552, 127.734, 128.189, 128.720, 129.039, 133.334, 134.184, 135.808, 136.749, 137.371, 151.621. Lit. ^{1}H NMR (***3-33***)[87] ($CDCl_3$) δ -0.22 (s, 9H), 1.72 (s, 2H), 1.82-2.68 (m, 4H), 5.43 (t, J = 4 Hz, 1H), 6.78-7.0 (m, 4 H). ^{1}H NMR ($CDCl_3$) (3,4-dihydro-1-(2H)-methylenenapthalene)[89] δ 1.9 (t, 2 H), 2.6 (br, 2H), 2.8 (t, 2H), 4.9 (s, 1H), 5.5 (s, 1H), 7.0-7.2 (m, 4H). ^{1}H NMR ($CDCl_3$) (1-naphthylmethyltrimethylsilane)[88] δ 0.0 (s, 9H), 2.57 (s, 2H). 7.10-7.93 (m, 7H). GC/MS *m/e* (rel intensity) of ***3-33***: 216 (M^+, 39), 201 (19), 142 (85), 73 (100). ***3-35***: 216 (M^+, 26), 201 (83), 142 (12), 73 (46), 59 (100). HRMS (***3-33***) calcd for $C_{14}H_{20}Si$: 216.1334, found: 216.1312.

2-Methyl-1-indanone *3-36*

Reaction # 1: 2-Methyl-1-indanone (0.5 g, 3.4 mmol) was subjected to the reaction conditions described in the general procedure. The resulting mixture was refluxed for 36 hours. After workup and solvent evaporation, distillation at 0.03 mm Hg and 35 °C, the reaction afforded of ***3-37*** (409 mg) in 55% yield. ^{1}H NMR (***3-37***) ($CDCl_3$) δ 0.168 (s, 9 H), 2.098 (s, 2H), 2.144 (s, 3H), 3.388 (s, 2H), 7.228-7.488 (m, 4H). ^{13}C NMR (***3-37***) ($CDCl_3$) δ -0.687, 14.520, 15.521, 42.338, 115.522, 122.802, 123.287, 125.716, 134.669, 142.576, 147.402.

Reaction # 2: Reaction was repeated and afforded a mixture (308 mg) of (3*H*-2-methylinden-1-ylmethyl)trimethylsilane ***3-37*** and 1-(trimethylsilylmethylidene)-2-methyl-3,3-dihydro-1*H*-indene ***3-38*** in 1:1 ratio, respectively, as determined by ^{1}H NMR. This corresponds to a 20 % yield of ***3-37*** and a 20 % of ***3-38***. ^{1}H NMR (***3-38*** *E/Z* isomers) ($CDCl_3$) δ 0.308 (s, 9H), 0.334 (s, 9H), 1.235 (d, J = 6.6 Hz, 3H), 1.301 (d, J =

6.9 Hz, 3 H), 2.639 (m, 2H, CHH, E/Z), 3.000 (m, 2H, CH_3CH, E/Z), 3.252 (m, 2H, CHH, E/Z), 5.644 (s, 1H), 6.604 (s, 1H), 7.154-7.609 (m, 8H, E/Z). ^{13}C NMR (***3-38*** *E/Z* isomers) ($CDCl_3$) δ -0.224, 0.330, 20.636, 23.625, 29.681, 37.360, 38.893, 39.242, 120.874, 124.228, 125.351, 125.898, 126.444, 127.309, 128.235, 128.462, 134.700, 135.762, 140.740, 141.301, 144.413, 146.537, 163.990, 164.324. ($CDCl_3$) GC/MS *m/e* (rel intensity) of ***3-37***: 216 (M^+, 98), 201 (37), 142 (64), 73 (100). ***3-38***: 216 (M^+, 11), 201 (4), 142 (100), 73 (55). HRMS (***3-37***) calcd for $C_{14}H_{20}Si$: 216.1334; found: 216.1337.

Preparation of 2-deuterio-2-methyl-1-indanone

To 100 mL schlenk flask equipped with a magnetic stir bar was added potassium hydride (1.25 g, 3 eq. of, 35 % in mineral oil). Potassium hydride was washed with 3 portions of 10 mL hexanes to remove mineral oil. Ether (20 mL) was introduced into the flask after washing and the resulting solution was cooled to 0 °C. 2-Methyl-1-indanone (0.5 mL, 3.64 mmol) was added dropwise to the KH solution through a syringe. The resulting yellow solution was stirred for two hours at 0 °C. It was quenched with 10 mL D_2O in the schlenk flask. After solvent evaporation, 0.4939 g (93% recovery) of 2-deuterio-2-methyl-1-indanone was isolated with 77 % deuteriation; it was determined by GC/MS. Percentage of deuteriation of 2-deuterio-2-methyl-1-indanone was determined by ^1H NMR as well, it was found to be 90 %. ^1H NMR (C_6D_6) δ 1.056, (s, 3H), 2.1235 (d, J = 17.1 Hz, 1H), 2.7195 (d, J = 17.1 Hz, 1 H), 7.0475 (m, 3H), 7.7905 (d, J = 7.5 Hz, 1H). ^{13}C NMR (C_6D_6) 16.112, 34.732, 41.864 (t), 124.024, 126.543, 127.408, 134.192, 137.075, 153.237, 207.595. ^1H NMR (C_6D_6) (2-methyl-1-indanone) δ 1.064, (2, J = 7.2 Hz, 3H), 2.121 (dd, J = 4.2, 16.8 Hz, 1H), 2.250 (m, 1 H), 2.718 (dd, J = 7.8, 16.95 Hz),

7.0475 (m, 3H), 7.7905 (d, J = 7.5 Hz, 1H). GC/MS *m/e* (rel intensity) of 2-deuterio-2-methyl-1-indanone: 147 (46), 132 (100).

Reaction of 2-deuterio-2-methyl-1-indanone

2-Deuterio-2-methyl-1-indanone (250 mg, 1.7 mmol) was subjected to the reaction conditions described in the general procedure. The resulting mixture was refluxed for 36 hours. Workup afforded a mixture (172 mg) of allylsilane ***3-36*** and vinylsilane ***3-38*** in a 1:1.4 ratio, respectively, as determined by ^{1}H NMR. This corresponds to a 19 % yield of ***3-36*** and a 26 % of ***3-38***. Percentage of deuteriation of allylsilane was determined by GC/MS and ^{1}H NMR. It was found to be 42 % deuteriation by GC/MS and 32 % deuteriation by ^{1}H NMR (it was determined by comparisons of the benzylic proton signal with the peak area of methyl C**H**$_3$, methylene C**H**$_2$TMS and TMS peak areas).

4-Methoxyphenyl methyl ketone *3-42*

4-Methoxyphenyl methyl ketone (0.5 g, 3.3 mmol) was subjected to the reaction conditions described in the general procedure. The resulting mixture was refluxed for 36 hours. After workup and solvent evaporation, distillation at 76 °C, 0.03 mm Hg, to afford of (2-(4-methyoxyphenyl)allyl)trimethylsilane[98] ***3-43*** (431 mg) in 59% yield. ^{1}H NMR (***3-43***) ($CDCl_3$) δ -0.038 (s, 9 H), 2.042 (s, 2H), 3.832 (s, 3H), 4.837 (s, 1H), 5.118 (d, J = 0.82 Hz, 1H), 6.829 (d, J = 8.8 Hz, 2H), 7.391 (d, J = 8.5 Hz, 2H). ^{13}C NMR (***3-37***) ($CDCl_3$) δ -1.431, 26.069, 55.086, 108.475, 113.317, 127.309, 135.125, 145.778, 158.860. Lit. ^{1}H NMR (***3-43***) δ -0.12 (s, 9H), 1.96 (s, 2H), 3.79 (s, 3H), 4.75 (s, 1H), 5.03 (d, J = 1.5 Hz, 1H), 6.81 (d, J = 8.8 Hz, 2H), 7.31 (d, J = 8.8 Hz, 2H). GC/MS *m/e* (rel

intensity) of ***3-43***: 220 (M^+, 12), 205 (54), 165 (7), 73 (100). HRMS (***3-43***) calcd for $C_{13}H_{20}SiO$: 220.1283; found: 220.1286.

Preparation of p-methoxyphenylcyclohexylmethanol

To 100 mL schlenk flask equipped with a magnetic stir bar was added magnesium (1.63 g, 68 mmol), 30 mL THF and cyclohexyl chloride (3.23 g, 27 mmol, 2.5 eq. of). The resulting mixture was allowed to reflux for one hour. After cooling at room temperature, p-methoxybenzaldehyde (2.21 mL, 18 mmol) was added to the grignard reagent. The resulting solution was allowed to reflux for another one hour. After reflux, reaction was quenched with 10 % cold H_2SO_4 and extracted with ether. Ether solution was dried over $MgSO_4$ for half an hour. After solvent evaporation, 3.4 g (87%) of p-methoxyphenylcyclohexylmethanol was isolated (m.p. 84-85 °C).^{1}H NMR ($CDCl_3$) δ 0.809-1.982 (m, 12H), 3.795 (s, 3H), 4.290 (d, J = 7.5 Hz, 1 H), 6.863 (d, J = 8.7 Hz, 2H), 7.239 (d, J = 8.4 Hz, 1H).

Oxidation of p-methoxyphenylcyclohexylmethanol

To a 50 mL round bottom flask, p-methoxyphenylcyclohexylmethanol (2 g, 9.8 mmol), PCC (2.94 g 13.6 mmol) and 10 mL CH_2Cl_2 was added. The reaction was allowed to stir overnight. The resulting mixture was filter through silica gel pad twice and washed with anhydrous ether. Solvent evaporation afford p-methoxyphenylcyclohexylketone[99] ***3-48*** (1.56 g, m.p. 66-68 °C) in 73 % yield. ^{1}H NMR ($CDCl_3$) δ 1.096-1.785 (m, 10H), 3.134 (m, 1H), 3.770 (s, 3H), 6.844 (d, J = 9 Hz, 2H), 7.851 (d, J = 9 Hz, 2H). ^{13}C NMR ($CDCl_3$) 25.841, 29.483, 45.236, 55.328, 113.635, 130.405, 163.155, 202.295. Lit. ^{1}H NMR δ 1.12-2.22 (m, 10 H), 2.92-3.24 (m, 1H), 3.82 (s, 3H), 6.82 (d, J = 9 Hz, 2H), 7.84 (d, J = 9 Hz, 2H).

4-Methoxyphenyl cyclohexyl ketone *3-48*

4-Methoxyphenyl cyclohexyl ketone (0.5 mL, 3.8 mmol) was subjected to the reaction conditions described in the general procedure. The resulting mixture was refluxed for 48 hours. After solvent evaporation, reaction afforded mixture of products (667 mg). GC/MS data indicated the presence of five products; four of which have a molecular mass of 288.5 g/mol and one has a molecular mass of 216.32 g/mol. They are tentatively assigned as ***3-49***, ***3-50***, ***3-51 E/Z***, ***3-52***. Yields were not determined due to the complexity of the spectra. ^{1}H NMR ($CDCl_3$) (mixture) δ -0.211 (s, 9H, ***3-51***), 1.075-2.422 (m, 11H, mixture), 3.790 (s, 3H, mixture), 4.921 (s, 1H, ***3-50***) 5.073 (s, 1H, ***3-50***) 5.472 (s, 1H, ***3-51***), 7.055 (m, 5 H, mixture). ^{13}C NMR ($CDCl_3$) (mixture) 0.163, 26.312, 26.463, 26.736, 26.873, 32.291, 32.777, 42.565, 48.879, 55.101, 55.161, 109.052, 112.785, 113.468, 123.970, 127.567, 129.510, 136.627, 154.277, 158.435, 164.658.

Preparation of 5-hydroxy-5-phenyl-10,11-dihydro-5 *H*-dibenzo[*a,d*]cyclohepten *3-52*

To 100 mL schlenk flask equipped with a magnetic stir bar was added magnesium (0.47 g, 19 mmol), 30 mL THF and bromobenzene (2.11 g, 13 mmol, 1.4 eq. of). The resulting mixture was allowed to reflux for one hour. After cooling at room temperature, dibenzosurberone (2 g, 9.6 mmol) was added to the Grignard reagent. The resulting solution was allowed to reflux for another one hour. After reflux, the reaction was quenched with 10 % cold H_2SO_4 and extracted with ether. Ether solution was dried over $MgSO_4$ for half an hour. After solvent evaporation, 2.4 g (88%) of 5-hydroxy-5-phenyl-10,11-dihydro-5 H-dibenzo[a,d]cycloheptene ***3-52*** was isolated (m.p. 148-149 °C).[95] ^{1}H

NMR ($CDCl_3$) δ 2.366 (br, 1H), 2.681-2.957 (m, 4H), 7.025-8.107 (m, 14H). ^{13}C NMR ($CDCl_3$) δ 32.397, 125.533, 125.867, 126.565, 127.567, 127.704, 128.645, 130.526, 137.750, 143.472, 148.480.

Reaction of 5-hydroxy-5-phenyl-10,11-dihydro-5 *H*-dibenzo[*a,d*]cycloheptene *3-52*

5-Hydroxy-5-phenyl-10,11-dihydro-5*H*-dibenzo[*a,d*]cycloheptene (0.5 g, 1.7 mmol, 0.17 M in xylene) was deprotonated by n-butyllithium to generate the corresponding alkoxide anion at 0 °C, diethylaluminum chloride was introduced followed by addition of 0.1 eq. of water The resulting mixture was refluxed for 48 hours. After solvent evaporation, reaction afforded a mixture (457 mg) of 5-phenyl-5*H*-dibenzo[*a,d*]cycloheptene ***3-53***,[95] and 5-phenyl-10,11-dihydro-5*H*-dibenzo[*a,d*]cycloheptene ***3-54***[95] in a 3.4:1 ratio (^1H NMR; methine proton ratio), respectively, as determined by ^1H NMR. This corresponds to a 68 % yield of ***3-53*** and a 20 % yield of ***3-54***. ^1H NMR ($CDCl_3$) (***3-53***, purified by flash chromatography with 100 eq. of silver nitrate impregnated silica gel as stationary phase and hexanes as mobile phase). ^1H NMR (***3-53***) ($CDCl_3$) δ 5.368 (s, 1H), 6.574 (m, 1H), 6.715 (s, 2H), 7.041-7.488 (m, 13H). ^{13}C NMR ($CDCl_3$) δ 57.482, 125.795, 126.512, 127.085, 127.237, 128.512, 129.787, 130.409, 130.819, 134.674, 140.320, 141.822. HRMS (***3-53***) calcd for $C_{21}H_{16}$: 268.1252; found: 268.1233. Lit m.p: 141.5-142.5 °C; found: 130-135 °C.

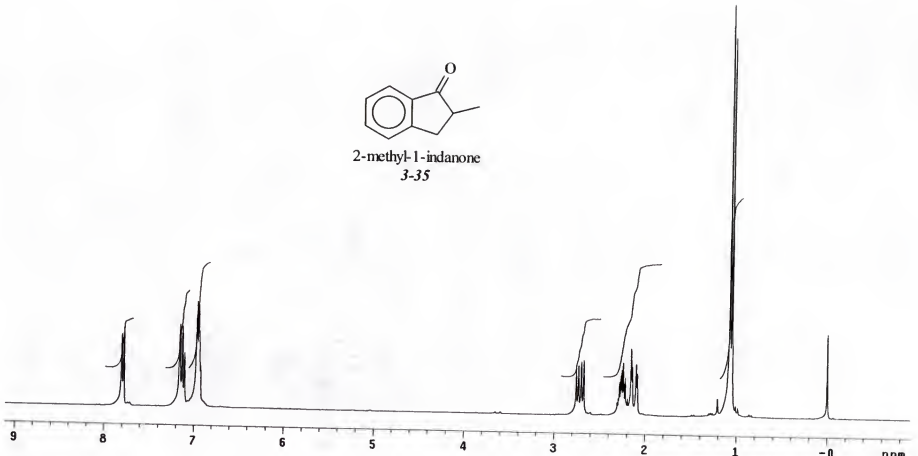
Hydrogenation of the product mixture

To 20 mL solution of ethyl acetate (degased by argon gas for 15 min and cooled 0 °C) in a round bottom flask, equipped with magnetic stir bar, was added the product mixture from above (50 mg) and palladium on charcoal (10 mol %, 40 mg). A balloon filled with H_2 gas was connected to the flask to provide a hydrogen atmosphere. The

reaction mixture was stirred for 2 days. Filtration and solvent evaporation afforded (40 mg), 90 % recovery of ***3-54***. ^{1}H NMR (***3-54***) ($CDCl_3$) δ 2.648 (m, H), 2.995 (m, 2H), 5.147 (s, 1H), 6.799-7.256 (m, 13H). (*3-54*) δ 32.196, 58.226, 125.659, 126.053, 127.222, 128.011, 130.773, 131.502, 139.819, 140.244, 145.480. (*3-54*) calcd for $C_{21}H_{18}$: 270.1409; found: 270.1408. Lit. m.p.:[95] 114-115 °C; found 109-112 °C.

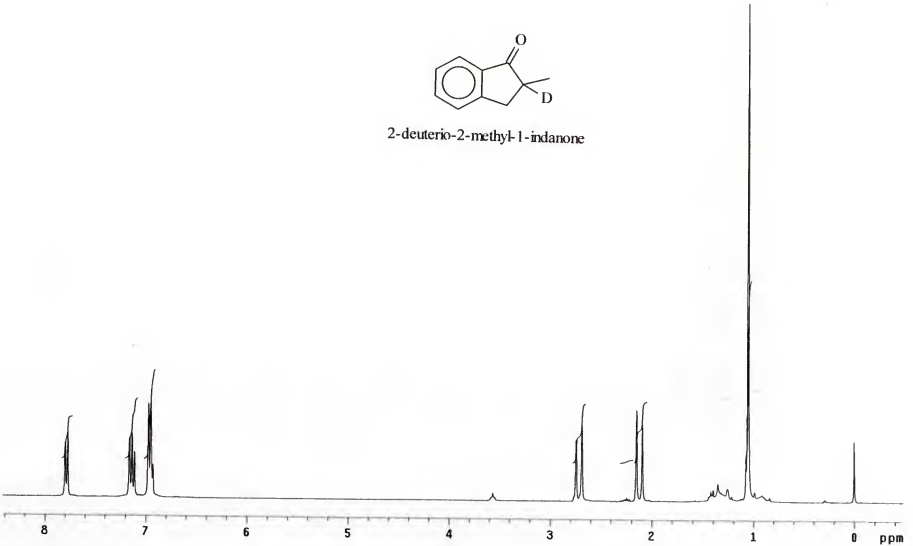
APPENDIX
SPECTRAL DATA

The ^{1}H and ^{13}C NMR spectra of selected compounds reported in Chapter 3 are shown in this appendix.

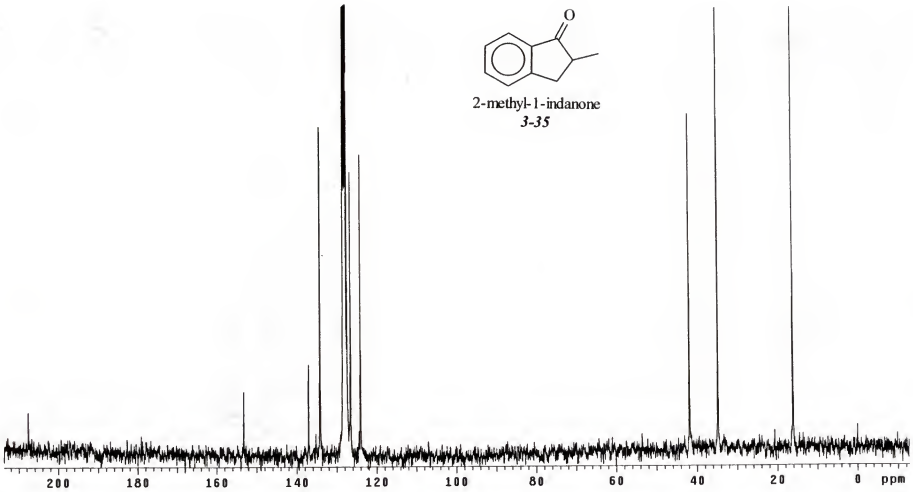


2-methyl-1-indanone

3-35



2-deuterio-2-methyl-1-indanone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120
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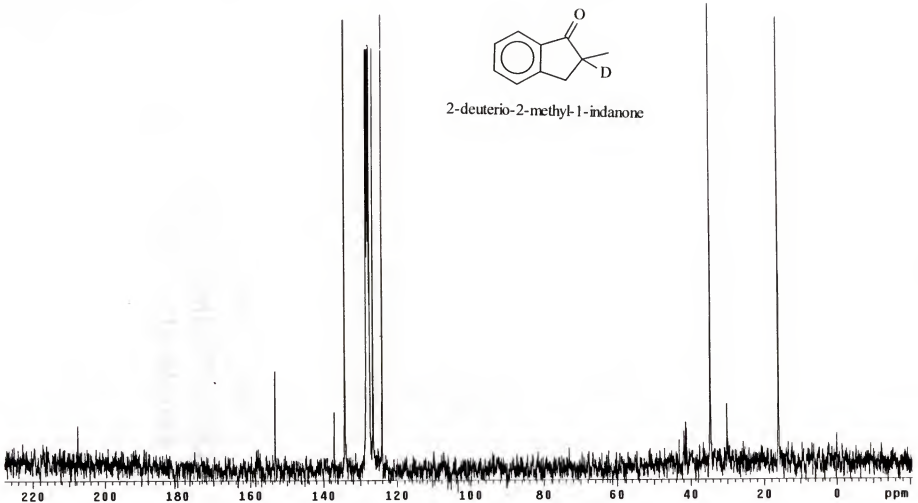
60
40
20
0
ppm



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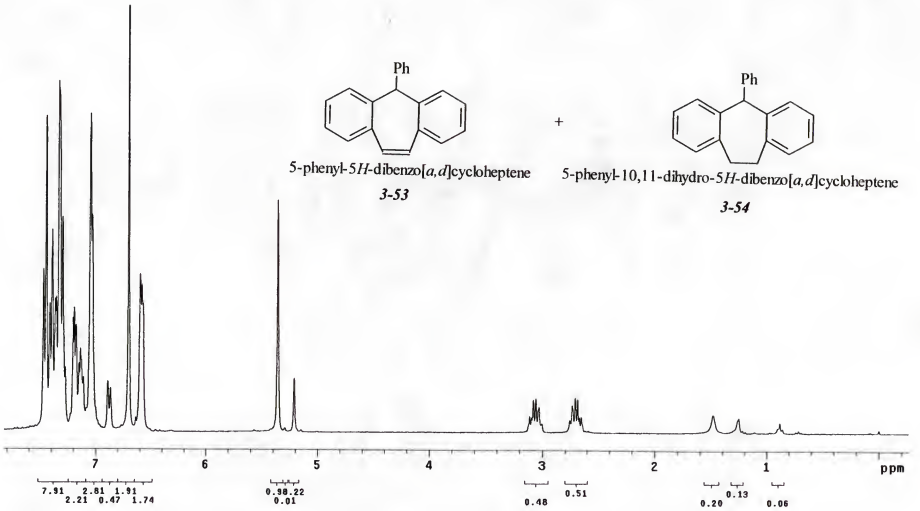


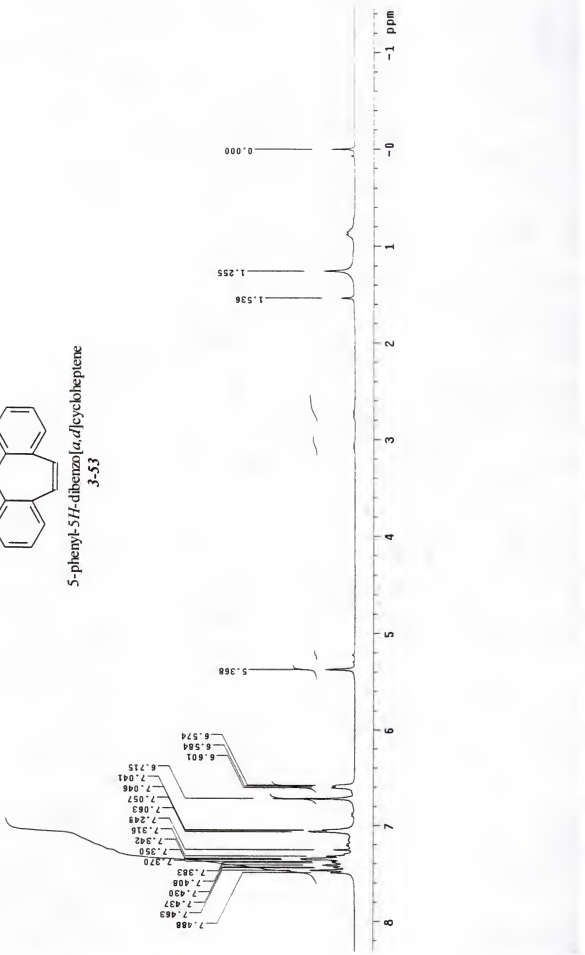
5-phenyl-5*H*-dibenzo[*a*,*d*]cycloheptene

3-53

\+

5-phenyl-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene

3-54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5-phenyl-5H-dibenzo[a,d]cycloheptene
3-53
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7.437
7.430
7.408
7.383
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7.350
7.342
7.316
7.249
7.063
7.057
7.046
7.041
6.715
6.601
6.584
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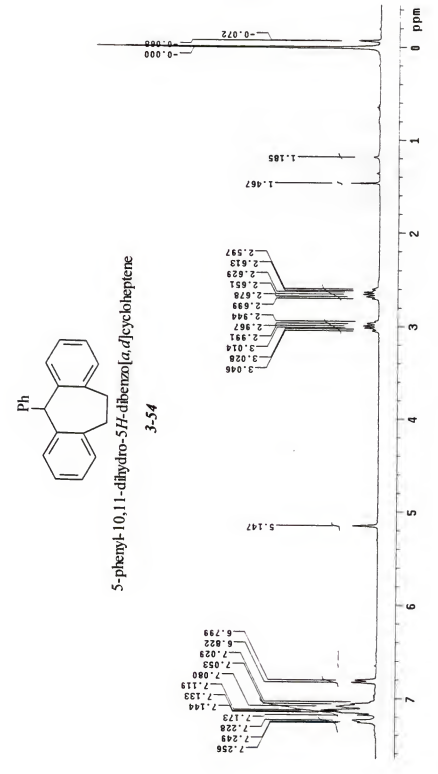

5-phenyl-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene

3-54

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BIOGRAPHICAL SKETCH

Man Lung (Desmond) Kwan was born in 1968 in Hong Kong. He is the son of a metal construction worker and a housewife. Due to a medical condition, he could not finish his high school work but came to the United States to further his study in chemistry at the University of South Alabama. Under the patient guidance of Dr. Norris Hoffman, Desmond decided to pursue graduate studies in chemistry. He received his B.S. degree from the University of South Alabama in 1993 and was admitted to graduate study at the University of Florida. He received Jesus as his savior and was baptized in 1994. In that same year he joined the research group of Dr. Merle A. Battiste and worked in the area of organoaluminum in organic synthesis.

On July 19, 1988, Desmond Kwan arrived in Dallas, Texas. He lived in Tyler Texas for a month and moved to Mobile, Alabama for undergraduate study. The first lesson he learned in Mobile was to take care of himself. He found it difficult to live in the United States unless he became independent; therefore, he dedicated himself to learn skills in different areas such as cooking, automobile repair and maintenance, martial arts, photography, English, and a variety of other areas. He thought life would become easier after becoming a talented person. His philosophy changed after he came to Gainesville, Florida. He tried to be in control of his life but he could not, because daily problems were too much for him to handle. He eventually realized there is a partner who always stands by him and wants to help. Desmond had never allowed

God to help because he was so focused on himself. He was lost but now is found. Desmond eventually found the power of living. He received God as his savior. Since then his life was not getting any easier, but he is not fighting alone; God is with him and became his partner. He believes people, including chemists, are never be inventors, they only discover what God has created. God is the only creator in the universe. If a frog see a table, he said it is natural; no one created the table. Is he correct? Looking around the universe, we said no one created all this. Are we right? Should we humble ourselves to admit there is a God?

"Does anyone ever bring in a lamp and put it under a bowl or under the bed? Doesn't he put it on the lampstand? Whatever is hidden away will be brought out into the open, and whatever is covered up will be uncovered. Listen then, if you have ears!" Mark 4: 21-25.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Merle A. Battiste, Chairman
Professor of Chemistry

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William R. Dolbier, Jr.
Professor of Chemistry

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David E. Richardson
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Tomas Hudlicky
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Kenneth B. Sloan
Professor of Medicinal Chemistry

This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

August, 1999

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